

**METAL-LIGAND EQUILIBRIA STUDIES
IN SOLUTION
(FORMATION EQUILIBRIA OF METAL COMPLEXES
INVOLVING DTPA LIGAND)**



**A THESIS SUBMITTED FOR
THE DEGREE OF**

Doctor of Philosophy
IN
Science

By
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M.Sc.

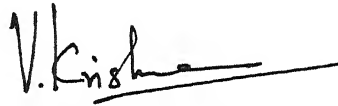
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SUPERVISOR'S CERTIFICATE

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DEDICATED TO
MY
GRANDFATHER
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INTRODUCTION

INTRODUCTION

Mixed chelation occurs commonly in biological fluids, as millions of potential ligands are likely to compete for metal ions found in vivo, i.e. sodium, potassium, magnesium, calcium, manganese, iron, cobalt, copper, zinc and molybdenum⁽¹⁾. It is well known that ternary coordination complexes play an important role in biological processes, as exemplified by many instances in which enzymes are known to be activated by metal ions^(2 to 9). Ternary complexes have also been implicated in the storage and transport of active substances through membranes and these phenomena are strongly dependent on the formation of such species and the nature of the involved metal ion.

The advent of polydentate ligands has completely revolutionized the field of co-ordination chemistry. The metal complexes formed with polydentate ligands, called metal chelates, have very high stability and sometimes selectively due to formation of many closed rings. The number of closed rings depends on the co-ordination number of the central metal ions and the structure of metal chelates depends upon the co-ordination geometry.

Mixed ligand-mixed metal complexes involving more than one metal ions of the same or of different types may prove as better models for multimetal – multiligand equilibrium occurring in the biological systems, such complexes are of importance in the study of bio-fluids particularly when hyperaccumulated metal ions are present for physiological or pathological reasons⁽¹⁰⁾. Mutual influences between metal ions may be of antagonist or of synergistic nature⁽¹¹⁾. Also the mixed-ligand mixed metal complexes are very common in enzymatic processes⁽¹²⁻¹³⁾.

Metal chelates play an important role in various fields of analytical⁽¹⁴⁻¹⁶⁾, biological⁽¹⁷⁻¹⁹⁾ and Industrial⁽²⁰⁻²²⁾ importance. Metals, which are essential for plants and animal nutrition, have been proved to form chelate with materials present in an organism. Thus chlorophyll, the green colouring matter of plant

is a magnesium chelate⁽²³⁾ and in haeme, the essential constituent of blood, is an iron chelate⁽²⁴⁾. Like haemoglobin most of the bioinorganic molecules have many donor sites. These bioinorganic molecules besides being co-ordinated to inorganic ions like Fe(II), Cu(II), Mg(II), macrocyclically still retain a number of potential binding sites, offering replacement of protons, leading to the formation of heteropolynuclear complexes. It has also been suggested ⁽²⁵⁾ that chelation plays a vital role in cancer and its cure.

OBJECTIVE AND IMPORTANCE

In recent years, a number of acyclic polyaminocarboxylic acid like Ethylenediaminetetraacetic acid (EDTA) and Diethylenetriaminepentaacetic acid (DTPA) have been developed for complexation of metal ions in vivo applications ⁽²⁶⁾. The anionic complexes of yttrium with EDTA and DTPA are rapidly protonated or attract other competing metal ions present in human serum (e.g. Ca^{2+} , Mg^{2+} , Zn^{2+}) to form mixed complexes ⁽²⁷⁾.

The polyaminocarboxylic acids have widely been used as antidotes ⁽²⁸⁻³¹⁾ in heavy metal detoxication, however, their hydrophilic nature renders them to be mostly distributed extracellularly. Metzler et al⁽³²⁾ have treated coronary artery disease with disodium EDTA and found improvements in their patients several months after ceasing therapy. Magnesium EDTA has been shown to give plaque reversals and to protect the aorta from atherosclerotic deposits in animals on atherogenic diets⁽³³⁻³⁴⁾.

The disodium salt of calcium EDTA complex is the drug for the treatment of Lead poisoning as the calcium in the chelate is easily replaced by the more strongly bound lead, which is readily excreted. It is also available in acute iron poisoning as also for the excretion of zinc and radioactive elements such as radioactive strontium.

The chelating agents are used in chemotherapy ⁽³⁵⁾, catalysis ⁽³⁶⁾, etc. Due to their interaction with metal ions to form metal chelates, or dislodging the bound metals and excreting these as soluble chelates from the system ⁽³⁷⁾

The chelating agent must be of low toxicity and not metabolized so as to persist unchanged in the biological system to perform their scavenging functions

Diethylenetriaminepentaacetic acid (DTPA), cyclohexanediaminetetraacetic acid (CDTA) and triethylenetetraaminehexaacetic acid (TTHA) have successfully been used in decorporating cadmium from the body of exposed animals⁽³⁸⁻³⁹⁾.

Very recently a comparison of the acute and chronic toxicity of DTPA and ferric DTPA complex has been reported. Indium-111 labeling of low density Lipoproteins with DTPA-BIS /Stearyl amide as potential/Radiopharmaceutical for tumor localization has been also studied ⁽⁴⁰⁻⁴¹⁾.

A number of metal ions such as Hg, Cd, As, Ca and Zn, etc. which are introduced in the environment through municipal and industrial wastes have toxic effect on biological systems ⁽⁴²⁾.

These pollutants injure or kill fish and other aquatic life and also render the water unfit for drinking or for industrial use. A prominent example is the occurrence of mercury in water. At one time it was believed that metallic mercury sinks into the sediments and remains there in chemically inert metallic form. But now it is known that anaerobic bacteria in bottom, muds, convert inorganic mercury to methyl mercury ($\text{CH}_3 \text{Hg}^+$) which can lead to mercury poisoning living beings. Cadmium is found in foods but the level is too low to be of any toxicological significance. Cadmium occurs in nature in association with zinc (Zn^{2+}) minerals. Growing plants require zinc and they also take up and concentrate cadmium with the same biochemical apparatus. The

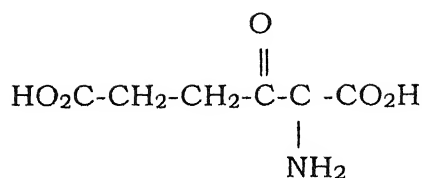
out break of cadmium poisoning occurred in Japan in the form of “itai itai” or “ouch ouch” disease. Many people suffered from this disease in which their bones became fragile. At high levels of cadmium causes kidney problems, anaemia and bone marrow disorders.

Lead is a relatively abundant metal in nature, occurring in lead minerals. In the atmosphere is relatively more abundant than other heavy metals. By far the major source of airborne lead is the combustion of leaded petrol/gasoline. Lead is added in the form of Tetraalkyl lead, primarily $\text{Pb}(\text{CH}_3)_4$ and $\text{Pb}(\text{C}_2\text{H}_5)_4$, together with the scavengers 1,2-dichloroethane and 1,2-dibromoethane. In common with other particulate pollutants, lead is removed from the atmosphere by wet and dry deposition processes. As a result, street dusts and road side soils become enriched with Pb, with concentration typically of the order 1000-4000 mg Kg^{-1} on busy streets.

It may be noted that most of the Pb in taken by a typical city dweller is from diet (about 200-300 μg per day), air and water adding further 10 to 15 μg per day each. Of this total intake, 200 μg of Pb is excreted while 25 μg is stored in the bone each day.

The major biochemical effect of lead is its interference with haeme synthesis, which leads to haematological damage. Lead inhibits several of the key enzymes involved in the overall process of haeme synthesis where by the metabolic intermediates accumulate. One such intermediate is delta-amino levulinic acid. An important phase of haeme synthesis is the conversion of delta-aminolevulinic acid to prophobilinogen. Pb inhibits the ALA-dehydrase enzyme (I) so that it cannot proceed further to form (II) prophobilinogen.

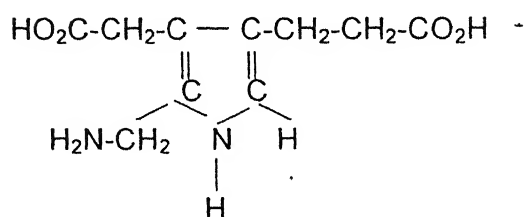
[1]



Delta - aminolevulinic acid

[ALA dehydratase: cytoplasm]

[2]



Porphobilinogen

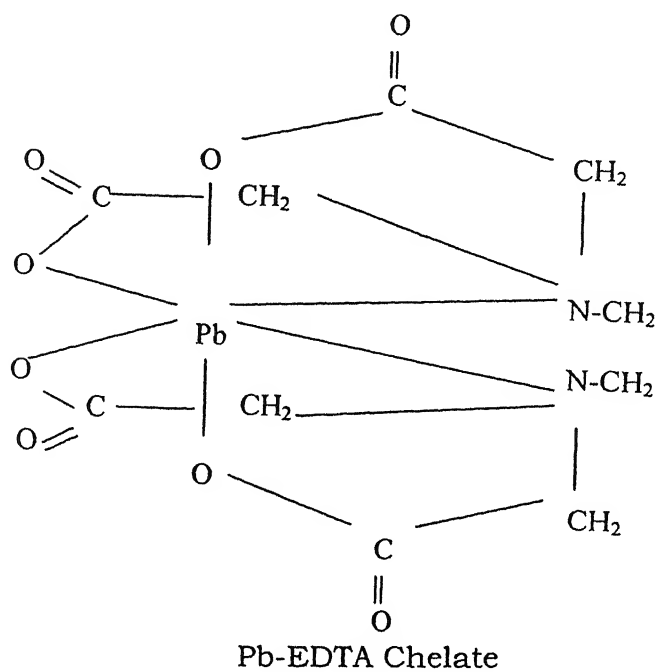
The overall effect is the disruption of the synthesis of haemoglobin as well as other respiratory pigments, such as cytochromes, which require heme. Finally, Pb does not permit utilization of O₂ and glucose for life-sustaining energy production. This interference can be detected at a head level in the blood of about 0.3 ppm. The detection of (I) provides a sensitive test for Pb in the body. At higher levels of Pb in the blood (> 0.8 ppm) there will be symptoms of anaemia due to the deficiency of haemoglobin. Elevated Pb levels (> 0.5 – 0.8 ppm) in the blood cause kidney dysfunction and finally brain damage.

Due to the chemical analogy of Pb²⁺ with Ca²⁺, bones act as repositories for Pb accumulated by the body. Subsequently, this Pb may be remobilized along with phosphates from the bones, which exert a toxic effect when transported to soft tissues.

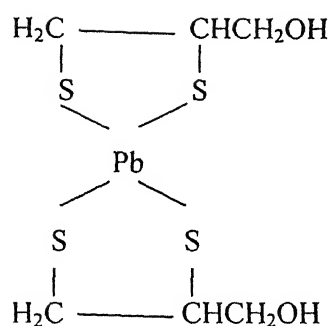
Lead poisoning can be cured by treatment with chelating agents⁽⁴³⁾ which strongly bind Pb²⁺. Thus, calcium chelate in solution is fed to the victim of lead

poisoning; Pb^{2+} displaces Ca^{2+} from the chelate and the resulting Pb^{2+} chelate is rapidly excreted in the urine. Three typical Pb chelates are shown below

[3]



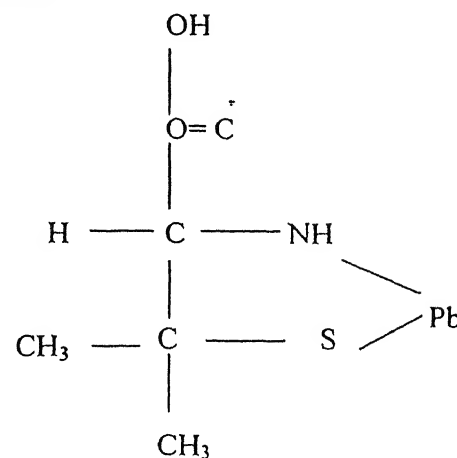
[4]



(BAL=2,3 dimercaptopropanal)

BAL, abbrev of British anti- lewisite chelate

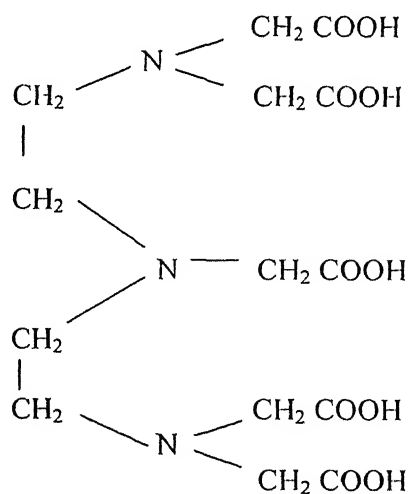
[5]



Zinc has an important biological role in the enzyme systems of animals and plants. Humans contain about 2 gm of zinc. This is the second largest amount of a transition metal after Fe, 4 gm. There are about 20 enzymes containing zinc in the body, which are responsible for proper absorption of Co_2 by red blood cells in muscles and other tissues and for maintaining proper pH in the muscles and tissues.

Some of the zinc containing enzymes play an important role ⁽⁴⁴⁾ in the digestion of protein by animals. Besides this, zinc enzymes are also involved in the energy release processes, sugar metabolism and metabolism of alcohol in the human body.

The choice of Diethylenetriaminepentaacetic acid (DTPA) has been prompted by the consideration that it is a polydentate ligand having eight donor atoms. It behaves as an octadentate ligand and thus possesses a high degree of freedom and should be able to occupy ⁽⁴⁵⁾ all coordination positions. However, when DTPA coordinates with metal ions having lower coordination numbers, some of the coordination positions of DTPA are left free.



[1 1]

DTPA (Diethylenetriaminepentaacetic acid)

Since the use of DTPA and other polyaminocarboxylic acids as sequestering agents ⁽⁴⁶⁾ in biological and industrial processes involves the presence of more than one type of metal ions in diverse concentrations, hence the chances of mixed chelation required to be investigated

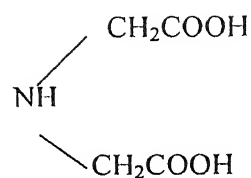
On the basis of relative protonated constants of several metal DTPA binary complexes, it has been observed ^(47,48) that $H_3 Hg (II)$ DTPA complexes is most stable and a versatile ligand for further interactions with other metal ions leading to the formation of heterobinuclear complexes

REVIEW ON METAL COMPLEXES OF POLYAMINOCARBOXYLIC ACIDS WITH SPECIAL REFERENCES TO METAL LIGAND EQUILIBRIA IN SOLUTION

The polyaminocarboxylic acids serve as multidentate ligands, coordination occurring through the amino nitrogen and oxygen of carboxylate group. Some of the important polyaminocarboxylic acids are

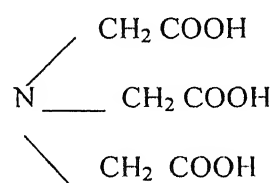
- 1 Iminodiacetic acid (IMDA)
- 2 Nitrilotriacetic acid (NTA)
- 3 Ethylene diamine tetra acetic acid (EDTA)
- 4 Cyclohexane diamine tetra acetic acid (CDTA)
5. Diethylene triamine penta acetic acid (DTPA)
6. 1,2, Propylene diamine tetra acetic acid (PDTA)
7. Triethylene tetra amine hexa acetic acid (TTHA)

These polyaminocarboxylic acid are well known to act as polydentate chelating agents and form very stable metal chelates. Thus they occupy a sufficiently good number of coordination positions, available on the metal ions, e.g. IMDA (1 2) acts as a tridentate ligand with alkaline earth metal ions it forms only a 1:1 chelate⁽⁴⁹⁾ but with transition metal ions it forms both 1:1 and 1:2 complexes⁽⁵⁰⁾.



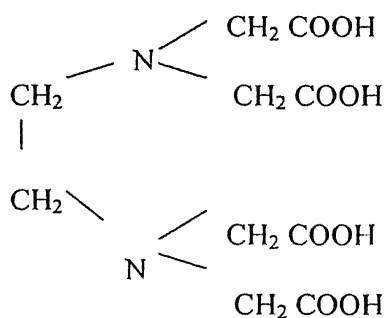
(1.2)

NTA (1.3) is a tridentate ligand and its metal chelates have been studied by Schwarzenbach et al.⁽⁵¹⁻⁵³⁾. It is observed that it usually forms a 1:1 metal chelate, normally occupying four coordination positions.



(1.3)

Among many polyaminocarboxylic acids that have been synthesized so far, the Ethylenediaminetetraacetic acid (1.4) still seems to hold pride of place. It is one of the polydentate ligands studied for a variety of purposes and extensively for its metal complexation reactions. Complexes of EDTA are formed at fairly low pH values and remain stable even in the higher pH range. Considerable work on proton ligand and metal – ligand equilibria of EDTA in a number of binary complexing systems have been reported⁽⁵⁴⁻⁶⁹⁾.

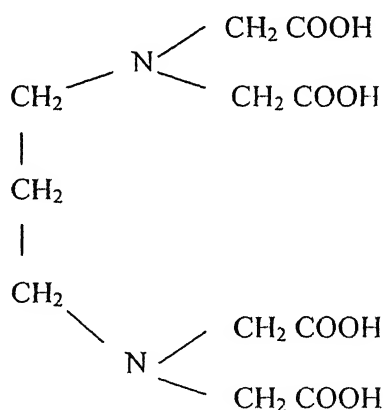


(1.4)

EDTA is a hexadentate ligand as having four oxygen and two nitrogen atoms through which it can bind a metal ion. The function of EDTA as a hexadentate chelating agent was postulated earlier ⁽⁷⁰⁾ in the study of its complexes. Pfeiffer and co-workers ⁽⁷¹⁻⁷²⁾ isolated alkaline earth metal complexes of EDTA.

The uncertainty in the structure of these complexes was painted out by Sawyer and Paulsen ⁽⁷³⁾. EDTA forms very stable metal chelates with practically every metal in the periodic table and almost invariably in the metal ion to ligand ratio as 1 : 1.

1,2 Propylenediamine tetraacetic acid (PDTA) ⁽¹⁵⁾ offers excellent opportunities for elucidating reactions of metal complexes with poly amino carboxylic acids because of the presence of the asymmetric carbon atom.

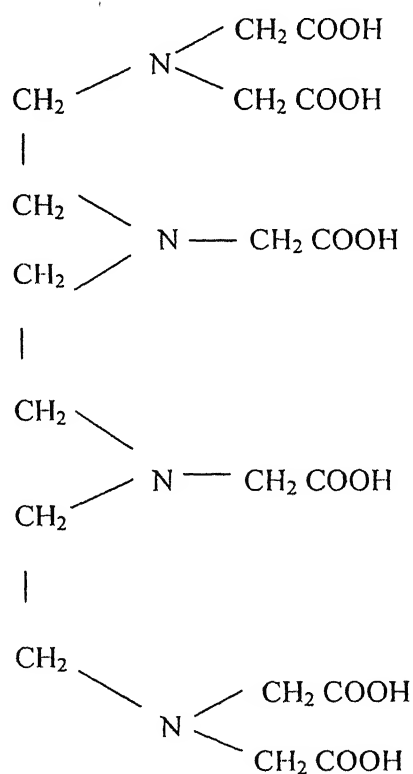


[15]

The ability of polyamino polycarboxylic acids to form generally stable and readily soluble complexes over the entire pH range with a variety of metal ions is the reason for their extensive and diversified application. In this development ethylenediaminetetraacetic acid (EDTA) played a central role and stimulated interest in the higher homologues, such as diethylene

triamine penta acetic acid (DTPA) or Triethylene tetraamine hexaacetic acid (TTHA)⁽¹⁻⁶⁾, in order to develop ligands with an increased affinity and selectivity for metal ions

Some of these complexes have been utilized as contrast enhancing agents in biological magnetic resonance imaging (MRI)⁽⁷⁴⁾ Among them the N-methyl glucamine salt of the gadolinium – DTPA complex (NMG)₂ [Gd (DTPA)], has been used clinically for this purpose for several years⁽⁷⁵⁾ This is the reason why lanthanide complexes with this ligand and its variously substituted derivatives have become the subject of extensive investigations in solutions⁽⁷⁶⁻⁷⁹⁾ and in the solid state⁽⁸⁰⁻⁸³⁾



(1.6)

Polyamino polycarboxylate ligands, both linear and cyclic, are currently used in medical applications to prepare metal compounds with radioisotopes for diagnostic imaging or radiotherapy or with lanthanides for magnetic resonance imaging (MRI)⁽⁸⁴⁾. These compounds combine favorable properties required in clinical use: high water solubility, low toxicity; high thermodynamics and kinetic stabilities. To expand their clinical applications, new chelates have been designed using functionalized polyamino polycarboxylate ligands. The functionalization can be used to increase the selectivity of the ligand and the stability of the metal chelates but also to optimize the hydrophilic/lipophilic balance or covalently attach the ligand to a synthetic supramolecular support or to a protein. These last two possibilities are essential to increase the intracellular bio-distribution of the compound and the diagnostic and radio therapeutic targeting of disease sites with high specificity⁽⁸⁵⁾.

To take advantage of the tumor cell's affinity for low density lipoproteins (LDL) to improve the delivery of imaging agents to tumor sites^(86,87)

Formation of mixed ligand complexes⁽⁸⁸⁻¹⁰⁰⁾ and their applications in analytical chemistry⁽¹⁰¹⁾, biochemistry⁽¹⁰²⁾ and environmental chemistry⁽¹⁰³⁻¹⁰⁴⁾, have been extensively studied. A number of mixed ligand complexes of several metal ions have been studied with some polyaminocarboxylic acid, viz, EDTA, NTA and IMDA⁽¹⁰⁵⁻¹⁰⁸⁾. Ethylene glycol-bis-2-aminoethylenetetraacetic acid (EGTA) is an octadentate polyamino carboxylic acid and forms stable binary complexes with many metal ions at low pH⁽¹⁰⁹⁻¹¹¹⁾. Thompson and Loras⁽¹¹²⁻¹¹³⁾ studied the formation of mixed complexes of lanthanides formed with HEDTA and IMDA.

Martell et al⁽¹¹⁴⁻¹¹⁶⁾ studied the formation of several mixed ligand chelates of Zr(IV), Th(IV) and U(IV) employing EDTA, NTA, CDTA, HEDTA and HIMDA as primary ligands and iron, salicylic acid, sulfo-salicylic acid pyrocatechol and 8-hydroxyquinoline as secondary ligands. These mixed ligand chelates:

are much more resistant to hydrolysis, olation and polymerization reactions than 1:1 simple chelates. Rana and Tandon⁽¹¹⁷⁾ studied some mixed ligand chelates of lanthanides as Pr(III), La(III) and Nd(III) with NTA as a primary ligand.

Limaye and Saxena⁽¹¹⁸⁻¹²⁰⁾ have investigated the formation of mixed ligand complexes of some lanthanides with EDTA as primary ligand and a variety of secondary ligands as aliphatic and aromatic carboxylic acid, amino acids, etc. And underlined the role of entropy in the stabilization of ternary complexes. Ternary thorium complexes with NTA, HEDTA and EDTA as primary ligands and schiff bases as secondary ligands have recently been reported⁽¹²¹⁾.

Studies on interaction of DTPA with zirconium(IV) indicate the formation, in solution, of a 1:1 complex in which all eight coordination positions about the metal atom are probably occupied by the eight donor atoms of the DTPA⁽¹²²⁾. Similarly, in the 1:1 Th(IV) chelate, DTPA is probably⁽¹²³⁾ functioning as an octadentate.

Very recently multinuclear N.M.R. study on the structure and dynamics of lanthanide (III) complexes of sugar-based DTPA-bis (amides) and cyclic DTPA derivatives in aqueous solution has been reported⁽¹²⁴⁻²⁵⁾. Temperature and pH dependence XAFS study of Gd(DTPA)₂ complex has also been studied and thus its solid state and solution structures have been established just now⁽¹²⁶⁾.

Sharma et al have thoroughly and systematically studied the mixed ligand complexes of rare earth with NTA⁽¹²⁷⁾, HEDTA⁽¹²⁸⁾, CDTA^(129,130) and DTPA^(131,132) and H₂KGA⁽¹³³⁾. Complexes having more than one central metal ion are termed as polynuclear complexes and the reason of their formation is that the ligand bound to the metal ion has still the ability to donate lone

pair(s) of electrons. Very often the ligand serves as a bridge between the central metal ions leading to the formation of M_2L type complexes

Mahapatra et al⁽¹³⁴⁻¹³⁷⁾ reported a large number of polymetallic complexes of ONNO and ONON donor chelating bis bidentate azodye with Co(II), Ni(II), Cd(II) and Hg(II).

The formation of heteroligand binuclear chelates of some transition metals with DTPA as the primary and diamine as the secondary ligand using potentiometry and spectrophotometry have also been studied in solution equilibria^(138,142).

The literature survey reveals that the complex formation, has been carried out mostly on mixed ligand chelates during the last decades, but the mixed metal complexes have received very little attention. However, there are a few references regarding mixed metal complexes as well as multimetal – multiligand complexes.

Mukherjee et al⁽¹⁴³⁾ have also investigated multimetal-multiligand systems indicating that multimetal equilibria is very common in biological relevance. Mixed ligand complex formation equilibria⁽¹⁴⁴⁾ of metal ions with aminoacids and small peptides in the presence of typical ligands provide models for metal-protein interactions in metallo-enzymes Ternary complexes⁽¹⁴⁵⁾ consisting of a metal ion and two different ligands other than the solvent have provided very useful and simple models for understanding the roles of metal ions in biological systems

Mixed ligand⁽¹⁴⁶⁾ complex formation equilibria of cobalt, nickel, copper and zinc(II) with sulfapyridine, sulfadiazine and sulfathiazole as primary ligands and glycine, β -alanine and dl-methionine as secondary ligands. Penicillin⁽¹⁴⁷⁾ group of antibiotic drugs are known to be inhibit protein synthesis in bacteria by causing misreading of the genetic code⁽¹⁴⁸⁾.

Enzymes responsible for genetic information transfer require one or other of the biological metal ions for their reactivity and also for their structural integrity. Metal ions by their kinds or by their concentration or by both, may influence the conformation of the ribosome, where the protein synthesis takes place. Due to lack of our knowledge about the interactions of the antibiotic drugs with metal ions and the influence these to of the amino acids, small peptides, nucleic bases nucleosides and nucleotides, the literature is silent about the specific inhibitory roles plays by these drugs to the protein synthesis. Therefore, a systematic investigation on the interaction of biological metal ions with antibiotic drugs of the penicillin family in the absence and in the presence of the above biological ligands is planned throw some light upon the molecular mechanisms of action of these drugs

M.S.Nair et al⁽¹⁴⁹⁾ ternary complexes of Cu(II) containing imidazole and aminoacids have attracted much attention because of their biological importance. The ternary complex, L-histidine-Cu(II) albumin acts as an intermediate in the exchange of Cu(II) in blood between a macromolecule such as albumin and a low substance like an aminoacid. It was shown that the exchangeable portion of Cu(II) in blood plasma occurs mainly in the form of mixed ligand complexes. Much attention⁽¹⁵⁰⁾ has been paid by several workers to the study of model mixed ligand complexes in an effort to understand the nature of metal-ion complexation in biological process, investigations on the coordination chemistry of potentially tridentate ligands are of considerable interest to many researchers because such studies are closely connected with peptide and protein complex chemistry. Studies⁽¹⁵¹⁾ on mixed ligand complexes of Cu(II) containing imidazole may be considered as models for enzyme – metal ion substrate complexes. Studies on Cu(II) complexes⁽¹⁵²⁾ of amino acid, it has been found that the stability of these complexes is affected greatly by the size of the chelate ring formed and by the position and nature of the third donor group.

The ever increasing importance of ternary complexes⁽¹⁵³⁾ especially those involving ligands containing functional groups identical with those present in enzymes, viz, -COOH, -NH₂, -CONH, etc., is obvious from the application of such complexes in many analytical and biological reactions. A mixed (O,N) donor such as amino acids with its hard oxygen and relatively soft nitrogen donors will be able to form complexes with Ni(II), which lies in the border region between a hard and soft acceptor. The⁽¹⁵⁴⁾ initial complex formation between a transition metal ion and a dipeptide in a binary system results in a chelate involving N-amino and O-peptide atoms. A K Banerjee et al⁽¹⁵⁵⁾ the homo- and hetero-polynuclear complexes has seen extensive growth, stimulated by interest in other areas and has been comprehensively reviewed.

Jurriaan Huskens et al⁽¹⁵⁶⁾ recent interest in polyazamacrocyclic paramagnetic and radioactive metal ion chelates largely results from their biomedical applications such as (i) Magnetic resonance imaging (MRI) contrast agents (ii) shift reagents for N.M.R – active cations, and (iii) diagnostic and therapeutic radiopharmaceuticals. As a result of intensive investigations of the chemical (thermodynamic, kinetic, structural, spectral and electrochemical) and pharmacological properties of macrocyclic complexes a number of paramagnetic Gd(III) chelates are now used clinically as MRI contrast agents and some Y(III) chelates are useful bioconjugates for monoclonal antibody radioactive labeling.

Banerjee⁽¹⁵⁷⁾ et al have reported the alkaline earth- metal complexes with 2,5 dihydroxy -p-benzoquinone, naphthazarin and quinizarin.

Prakash⁽¹⁵⁸⁻¹⁶⁰⁾ et. al extensively carried out the synthesis and characterization of alkali and alkaline earth metal complexes with various potential ligands containing nitrogen and oxygen the hard atoms

Ibolya Torok et al the imidazole moiety ⁽¹⁶¹⁾ plays a particular role in the active center of a large number of (metallo) proteins. Model compounds mimicking the main features of active sites have long been used to characterize better the relation between structure and function of these enzymes. In this respect, many imidazole containing ligands (e.g. peptides, pseudopeptides, polyamines) have been studied from a coordination chemical point of view. The results revealed the exceptional coordinating ability of the imidazole ring and also that its position in a peptide chain is a determining factor regarding the structure of the complexes formed. These studies were mostly devoted to mimicking structural features of imidazole containing active centers, and paid less attention to functional mimicking. In case of most (Pseudo) peptides studied, however, the metal-promoted deprotonation of amide nitrogen in the presence of Cu^{II} , Ni^{II} or Zn^{II} occurs near the physiological pH, which is particularly rare in metalloproteins.

The presence of an imidazole moiety in the active center of proteins is often related to hydrolytic reaction, even in the absence of metal ions. One of the most abundant class of hydrolytic enzymes are the phosphatases, which hydrolyse phosphate ester bonds. They have extremely widespread use in biological system (i) preparation and hydrolysis of DNA and RNA (ii) Transfer of energy (ATP) (iii) Metabolic processes (glucolysis, synthesis of amino acids), (iv) Control of the blood sugar level and (v) Phosphorelation – dephosphorelation (one of the most important controls of the cell function)

In Zn^{II} – containing nucleases, metal-bound imidazole rings are always present. Recently, great efforts have been made to develop efficient artificial nucleases. Most of the nuclease model studies were made to attain greater hydrolysis rates, using metal ions (e.g. lanthanoids Co^{III}) ligands (most of them polyazamacrocycles) and test compounds (activated arylphosphate esters) which do not reflect the active center of nucleases and native substrates. Only a few metal complexes have been published having

structural similarities with the native enzymes. Labile metal complexes, containing bidentate ligands are generally considered less active than rigid ones in hydrolyzing phosphate esters, however good hydrolytic activity was reported in certain cases against activated (aryl)-phosphate esters.

PRESENT WORK

The present work basically deals with the formation stability and structures of homo and hetero binuclear complexes of Diethylenetriamine .pentaacetic acid (DTPA). The studies have been carried out in the solution state as well as in the solid state. The solution studies deals with the potentiometric studies of the formation of mixed metal complexes of DTPA with $\text{Pb}^{(\text{II})}$ and $\text{Zn}^{(\text{II})}$ involving the alkaline earth and transition metal ions viz $\text{Be}^{(\text{II})}$, $\text{Mg}^{(\text{II})}$, $\text{Co}^{(\text{II})}$, $\text{Ni}^{(\text{II})}$, and $\text{Cu}^{(\text{II})}$ and $\text{Cd}^{(\text{II})}$ respectively. The formation has been studied by Irving and Rossotti technique and the data of stability constant have been evaluated by SCOGS computer program ⁽¹⁶²⁾. The stability of $\text{Pb}^{(\text{II})}$ and $\text{Zn}^{(\text{II})}$ metal ions with DTPA ligand is found to be much higher in comparison to other metal ions under study. On the persual of protonation constants of metal DTPA binary complexes, it has been observed that $\text{Pb}^{(\text{II})}$ DTPA and $\text{Zn}^{(\text{II})}$ DTPA complexes are very stable. After co-ordination with metal ions viz $\text{Pb}^{(\text{II})}$ and $\text{Zn}^{(\text{II})}$, the ligand still have uncoordinated functional groups for further interactions with other metal ions. This leads to the formation of ternary chelates of type $\text{M}_1 \text{M}_2 \text{DTPA}$. Lead and Zinc is well known to form tetra coordinated complex, but the ligand still has vacant coordinated positions. Thus it can be safely inferred that $\text{Pb}^{(\text{II})}$ and $\text{Zn}^{(\text{II})}$ forms a binary complex with co-ordination leading to the formation of homo and hetero bimetallic complexes. The studies have been carried out at $37 \pm 1^\circ\text{C}$. The stability constants have been calculated by SCOGS computer program.

The solid state studies deals with the preparation and isolation of some mixed metal complexes of $\text{Pb}^{(II)}$ -DTPA and $\text{Zn}^{(II)}$ -DTPA with alkaline earth metal viz $\text{Mg}^{(II)}$, $\text{Ca}^{(II)}$, $\text{Sr}^{(II)}$, and $\text{Ba}^{(II)}$ respectively. There structural studies are conducted by elemental analysis, metal analysis and infrared spectra. On the basis of these studies the structure of all these complexes has been proposed.

Metal complexes play an important role in various fields as in heavy metal detoxication, as antidotes. The chelating agents are used in chemotherapy, catalysis, and sequestering agents in biological and industrial processes, involve the presence of more than one type of metal ions in diverse concentrations. Multimetal-multiligand equilibrium occurring in the biological systems, when hyper accumulated metal ions are present for physiological or pathological reasons and the mixed ligand mixed metal complexes are very common in enzymatic processes. The DTPA complexes are used for tumor analysis by the process of radiopharmaceuticals¹⁶³⁻¹⁶⁴.

The thesis comprises of five chapters viz introduction, experimental, formation equilibria of binary systems, formation equilibria of homobimetallic systems and formation equilibria of heterobimetallic systems. During the solution studies it was thought that whether these heterobinuclear complexes exist in solid state or not. To confirm it preparation of some mixed – metal complexes has been carried out in the solid state. The structure of these prepared complexes has been confirmed by elemental analysis, metal analysis, and IR spectral is an additional work which has been included in the thesis as appendix.

CHAPTER III

EXPERIMENTAL

POTENTIOMETRIC INVESTIGATION IN SOLUTION

It has been proved that potentiometry is still one of the most important methods to study the electro chemical behaviour⁽¹⁶⁵⁾ of equilibria of interaction of metal ions and ligands , where there is release of hydrogen ions accompanying the complexation reaction. In such cases, a glass electrode furnishes information on the H^+ ion concentration and thereby on the extent of complex formation.

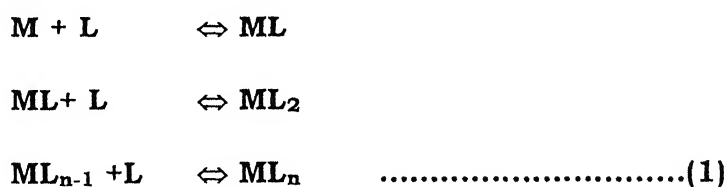
It is encouraging to note that the work reported in recent years has been contained merely to the collection of bulk of equilibrium data but elaborate theoretical treatments towards elucidation of metal ligand interaction in solution have also been carried out. Evidently, the scope of this fascinating field has become so broad that a comprehensive survey of literature has become almost an impossible task. An immense amount of equilibrium data is available in different published by Martell et al⁽¹⁶⁶⁻¹⁶⁸⁾.

2.1 THEORETICAL PRINCIPLES.

Stability of Metal Complexes.

The Calvin Bjerrum's pH titration technique modified by Irving and Rossotti⁽¹⁶⁹⁻¹⁷⁰⁾ has been used for the calculation of stability constants

The stability constant of a binary complex may be considered to take place as



Where n, is the number of multidentate ligand.

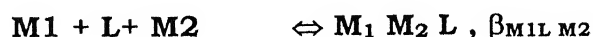
From the law of mass action

$$\begin{aligned}
 \frac{[M]}{[M][L]} &= k_1 \\
 \frac{[ML_2]}{[ML][L]} &= k_2 \\
 \frac{[ML_n]}{[ML_{n-1}][L]} &= k_n \dots\dots\dots(2)
 \end{aligned}$$

[] term refer to the activities of different species and k_1, k_2 and k_n are the stepwise stability constants. The 'overall stability constant' β_n is expressed as

$$\beta_n = \frac{[ML_n]}{[M][L]^n} \dots\dots\dots(3)$$

Ternary system (mixed metal and mixed ligand complexes) have attracted the attention of chemists mainly because of their important roles in biological systems. The effect of the structural features of the system, the effect of the structural features of the complex and the nature of the ligand on the stability of the ternary complexes and associated binary complexes is of great significance. The formation of heterobimetallic complexes can be considered to take place as-



$$\beta_{M_1 L M_2} = \frac{[M_1 M_2 L]}{[M_1][M_2][L]} \dots\dots\dots 4$$



$$k_{M_1 M_2 L} = \frac{[M_1 M_2 L]}{[M_1 L][M_2]} \dots\dots\dots(5)$$

one method of representing the stability of the ternary complex is in terms of –

$$\log k = \log k_{M_1 M_2 L} - \log k_{M_1 L}$$

i.e. the difference in the tendency of a ligand to bind to two free metal ions in solution. The value of log k depends upon the co-ordination number of metal ion, and the co-ordination position of the ligand⁽¹⁷¹⁾

2.2 COMPUTER PROGRAMME FOR CALCULATION OF EQUILIBRIUM CONSTANT.

The computer programs ⁽¹⁷²⁾ have been developed for calculating the stability constants of the metal complexes, from pH titration data. The more advanced of these programs use one of two mathematical approaches. The first is the non-linear least squares method, long used by crystallographers in the reduction of X-ray data. The technique has been applied to pH titration data for simple systems by the several co-workers⁽¹⁷³⁻¹⁷⁴⁾, but was expressed in more general computer programs by Rush-Johnson and Kraus and by Tobias⁽¹⁷⁵⁾. The latter's programme has since been developed and its efficiency improved⁽¹⁷⁶⁾. The modified programme which was called GAUSS has proved very useful in calculating the equilibrium constants of the various species present in solution containing one metal and one ligand⁽¹⁷⁷⁻¹⁷⁸⁾.

In 1962 Izzi and Sillen⁽¹⁷⁹⁾ described the computer program KUSKA for calculating one kind of metal ion and one kind of ligand. The binary and

ternary complexes⁽¹⁸⁰⁾ has been calculated with the aid of the HALTAFALL computer program

The computer program MINQUAD ⁽¹⁸¹⁻¹⁸²⁾ has been widely used to calculate formation constant of species in solution equilibria from data obtained by potentiometric titration. As systems of ever increasing complexity have been examined it has become apparent that improvements are needed in order to deal with some chemically significant problems of current interest

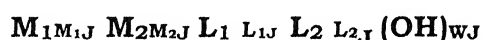
The developed a new program, SUPERQUAD ⁽¹⁸³⁾, which has been designed to SUPER cede mini QUAD by providing the facilities identified above in addition to those offered previously. The new program was evolved from MIQUV ⁽¹⁸⁴⁾ via the unpublished program BETAREF in which analytical formulae were used for all derivatives, but modifications have been so extensive that little of the original code remains intact. A related paper gives an illustration of the use of SUPERQUAD with impure synthetic tetrapeptides⁽¹⁸⁵⁾, those system defined analysis with the MINQUAD program.

Ropars and Viovy⁽¹⁸⁶⁾ described a program for one kind of metal ion and two different complexing agents, including the possibility of mixed complex formation and about the same time a program. Very soon afterward the much more general programs COMICS ⁽¹⁸⁷⁾

The program COMICS (Concentrations of metal ions and complex equilibria, such as mixed ligand or mixed and the usual stepwise (1·1, 1·2, etc) complexes, as well as protonated ligands and hydralysed metal ions. It uses a simple iterative procedure based on the fact for all positive values of X , $X^{1/2}$, is always closer to unity than X . The speed with which the method leads to convergence is less than for the conventional line or graphic methods, but this disadvantage is more than offset by the much simpler programming requirements and the greatly diminished amount of core storage that is necessary. In its first applications, COMICS was used to compute the

composition of a 10-metal-10-ligand system, involving 195 equilibrium constants (but omitting mixed complexes), and also of a 2-metal/3-ligand system comprising 28 species (including mixed complexes)⁽¹⁸⁸⁾ COMICS was primarily intended to make possible biological system, and hence to provide a background against which to view the reaction and equilibria in the living cell

In recent years a new computer program, SCOGS (Stability constants of generalization species) Which employs the conventional non- linear least-squares approach The program is written in FORTRANIV. It is capable of calculating k simultaneously, or individually, association constants for any of the species formed in system containing up to two metals and ligands, provided that the degree of complex formation is pH-dependent. The method can readily be extended to deal with more complicated system Thus SCOGS, like GAUSS, may be used to analyse appropriate pH titration data to yield acid association constants (and hence pka's) , metal ion hydrolysis constants Stability constant of simple complexes (ML, ML₂, etc) and stability constants of polynuclear species M₁ M₂ L, M₁ L₁ L₂ MLOH etc). In addition SCOGS may be used to different metals or two different ligands In fact , for a mixture of two metals M₁ M₂ and two different ligands L₁, L₂, association constant may be calculated with the program for any species j which can be described by the general formula



Where M_{1J} M_{2J} L_{1J} L_{2J} are positive intergers, or zero and WJ is a positive integer (for a hydrolysed species), zero or a negative integer (for a protonated species). The constant calculated in the overall formation constant β_j given by the expression

$$\beta_j = \frac{[M_1]^{M_{1j}} [M_2]^{M_{2j}} [L_1]^{L_{1j}} [L_2]^{L_{2j}} (OH)^{w_j}}{[M_1]^{M_1^j} [M_2]^{M_2^j} [L_1]^{L_{1j}} [L_2]^{L_{2j}} \{OH\}^{w_j}}$$

Where square brackets[] denotes concentrations and braces{ } denotes activities

The main program deals with the input of data, the setting up and solution of the least squares calculation and the output of results. Thus this programme has been successfully used in the refinement of data i.e (actual titre of base)- (titre calculated from input data using current estimates of the constants and the experimental value of pH).

Table 2.1

Stoichiometries of $(M_1)_p$, $(M_2)_q$, $(L_1)_r$, $(L_2)_o$, $(OH)_t$,

Complexes in the ternary M_1 = Primary metal Species i.e. $Zn^{(II)}/Pb^{(II)}$

M_2 = secondary metal species i.e. $Be^{(II)}$, $Mg^{(II)}$, $Ca^{(II)}$, $Sr^{(II)}$, $Ba^{(II)}$, $Co^{(II)}$, $Ni^{(II)}$ or $Cd^{(II)}$

STOICHIOMETRY					
$(M_1)_p$, $(M_2)_q$, $(L_1)_r$, $(L_2)_o$, $(OH)_t$,	M_1	M_2	L_1	L_2	OH
LH	0	0	1	0	-1
LH ₂	0	0	1	0	-2
LH ₃	0	0	1	0	-3
LH ₄	0	0	1	0	-4
LH ₅	0	0	1	0	-5
M_1 (II)-L	1	0	1	0	0
M_2 (II)-L	0	1	1	0	0
M_1 (OH) ⁺	1	0	0	0	1
M_2 (OH) ₂	1	0	0	0	2
M_1 (OH) ⁺	1	0	0	0	1
M_2 (OH) ₂	0	1	0	0	2
M_1 L (OH)	1	0	1	0	1
M_2 L (OH)	0	1	1	0	1
M_1 (II) – L- M_2 (II)	1	1	1	0	0

2.3. EXPERIMENTAL DETAILS

The present work is concerned with the potentiometric studies of ternary complexes of DTPA with different metal ions at a fixed temperature. Here the experimental procedure is briefly outlined.

MATERIALS USED

(i) Double Distilled Water.

Double distilled water is thoroughly boiled to expel CO_2 , cooled and stored in well stoppered containers. Double distilled water was used for rinsing the apparatus preparing different solutions and washing electrodes through out the experiment.

(ii) Sodium Nitrate (A.R.):

1M stock solution sodium nitrate was prepared and used to maintain the constant ionic strength.

(iii) Nitric Acid:

1M/ 0.2M stock solution of nitric acid was prepared and standardized against a carbonate free sodium hydroxide solution. The dilute solution of required strength were obtained from this stock solution.

(iv) Sodium Hydroxide Solution:

1M sodium hydroxide solutions are prepared in double distilled water. This solution is standardized against a standard oxalic acid solution. Sodium hydroxide solution is used as a titrant.

(v) Ligand Solution.

0.1/0.01 mol dm⁻³ solution of Diethylenetriaminepentaacetic acid (DTPA) (BDH) was prepared by dissolving it into two equivalent of alkali solution, which was prepared in double distilled water and had earlier been standardized against a standard oxalic acid solution

(vi) Metal Ion Solutions:

The following metal ions were used in the present study of complex formation-

- (1) Lead nitrate (A.R.)
- (2) Zinc nitrate (A.R.)
- (3) Beryllium nitrate (A.R.)
- (4) Magnesium nitrate (A.R.)
- (5) Calcium nitrate (A.R.)
- (6) Strontium nitrate (A.R.)
- (7) Barium nitrate (A.R.)

0.01 M solution of the above metal ions were prepared and standardized by EDTA titration.

Instruments Used

(i) pH meter

pH measurements were done by electric digital pH meter (century model CP- 901-S) with a glass electrode supplied with the instrument and working on 220 volts/50 cycles stabilized by A.C mains. The pH meter has a reproducibility of ± 0.01 pH. It is conditioned monthly by

saturated potassium chloride solution was prepared using a twice recrystallised sample (BDH)

(ii) Calibration of pH Scale

The pH meter is calibrated with buffer solutions of pH 7 and pH 9.2 before starting each set of observations. The buffer solutions were prepared by dissolving buffer tablets (BDH) in double distilled water. After completing the whole set, the calibration was again checked with buffer of pH 7.0 and found to be unaltered.

(iii) Titration Vessel.

The titration vessel was a specially designed double walled beaker of capacity 100 ml, made of pyrex glass. It is fitted with an inlet and outlet for circulation of water to maintain a constant temperature.

(iv) Thermostat.

An Altra- Thermostat type U₁₀ (VEB MLW) (Sitz Freital, Germany) was used to maintain a constant temperature in all the experiments.

(v) Conditions of Study

All the experiments were carried out in an atmosphere of purified nitrogen by bubbling it through the solution in which the electrode was dipping. The nitrogen gas thus served to prevent atmospheric oxidation and also to stir the solution.

TITRATION PROCEDURE

The following solutions were prepared keeping the total volume 50 ml in each case and the molar ratio of primary metal, secondary metal

and ligand are formed to the homo & hetero bimetallic complexes as follows –

Sol. A: 5 ml HNO_3 (0.02 M) +5 ml NaNO_3 (1M)+40 ml water

Sol. B 5 ml HNO_3 (0.02 M) +5 ml NaNO_3 (1M)+5 ml DTPA(0.01) +3.5 ml water

Sol. C 5 ml HNO_3 (0.02 M) +5 ml NaNO_3 (1M)+5 ml DTPA(0.01M) +5 ml $\text{M}_1(\text{II})$ (0.01M) +30 ml water

Sol. D 5 ml HNO_3 (0.02 M) +5 ml NaNO_3 (1M)+5 ml DTPA(0.01M) +10 ml $\text{M}_1(\text{II})$ (0.01M)+25 ml water

Sol. E 5 ml HNO_3 (0.02 M) +5 ml NaNO_3 (1M)+5 ml DTPA(0.01M) +5 ml $\text{M}_2(\text{II})$ (0.01M) +30 ml water

The ionic strength of all mixtures solutions described above, was kept 0.1 M sodium nitrate. The free acid concentration was also kept equal in each case at 0.002 M. These solutions were individually titrated against carbonate free standard sodium hydroxide solution, and temperatures 25 °C & 35 °C. The pH meter reading with progressive addition of alkali to the titration mixture were noted. When the pH scale was stabilized

CHAPTER III

FORMATION EQUILIBRIA OF BINARY SYSTEMS

The present chapter deals with the binary complexes formed by diethylenetriaminepenta acetic acid (DTPA) with Zn (II), Pb(II), Be(II), Mg(II), Ca (II) Sr (II) and Ba(II) system in aqueous medium at $37 \pm 1^\circ$ and $\mu = 0.1 \text{ mol dm}^{-3} \text{ NaNO}_3$. The relevant stability constants have been evaluated using SCOGS computer program.

Titration Procedure:

The reaction mixtures were prepared by keeping the total volume 50 ml in each case and the molar ratio of ligand and metals undertaken was kept 1 : 1.

Solution A: 10 ml NaNO_3 (1 mol dm^{-3}) + 10 ml HNO_3 (0.02 mol dm^{-3}) + 40 ml H_2O

Solution B: 5 ml NaNO_3 (1 mol dm^{-3}) + 5 ml DTPA (1 mol dm^{-3}) + 35 ml H_2O

Solution C: 5 ml NaNO_3 (1 mol dm^{-3}) + 5 ml HNO_3 (0.02 mol dm^{-3}) + 5 ml DTPA (1 mol dm^{-3}) + 5 ml M (II) (0.1 mol dm^{-3}) + 30 ml H_2O

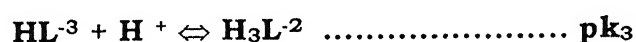
Where, M (II) is the metal ion of the various system mentioned above.

The Table 3 1 to 3 7 and the titration curves are shown in Figures 3 1 to 3 7 The plot of pH against the volume of alkali gives the titration curves A, B & C to acid, DTPA and M (II) –DTPA complex respectively

SPECIES DISTRIBUTION CURVES:

The plot of % concentration against pH gives the distribution curves of the species formed These distribution curves are obtained by running the computer program ORIGIN 4 0 and are shown in Fig 3 8 to 3 14 The distribution of binary system has been sketched and studied in order to explain the comparative chelating behaviour of the ligand towards both the metal ions under study.

The proton- ligand formation constants of DTPA determined by Irving- Rossotti titration technique⁽¹⁸⁹⁾ are given in Table 3 8 DTPA shows five replicable protons The proton –ligand formation constants reported in agree with the literature values Due to the presence of five coarboxylic groups, it behaves as penta basic acid Its protonation equilibria are expressed as



Metal –Ligand Formation Constants:

The table 3 10 represents the refined values of binary and hydroxo species of M (II) –DTPA system taken under study

The computer gives the values of the constants ($\log \beta_{pqts}$) and also the concentration distribution of the complex species at different pH values as the output described further

Zn (II) –DTPA system:

Fig 3 1 and fig 3 8 represent the titration curves and speciation curves respectively of the present binary system In this system 1 1 metal to ligand ratio in order to compare binary & ternary systems in the same metal to ligand ratios have been taken The species distribution curves reveal for the formation of following major species. H_3L , H_2L and Zn–DTPA

The formation of binary complex takes place by the following general equation



The species H_3L exists(70%) predominate in the pH range 2.5 to 4.0 while very small amount ($\approx 2\%$) of H_2L species exists in the pH range 2.5 to 3.5

Proton –ligand formation constants of DTPA and metal-ligand formation constants of Zn(II)-DTPA complex are given in table 3 8 and 3.10 (i) respectively.

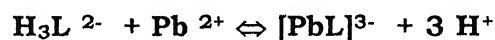
It is clear from the Fig 3 8 that the formation of Zn (II) –DTPA species starts from pH ~ 2.5 and there is a gradual increase in its concentration reaching up to ($\approx 99\%$) until become constant at pH ~ 4.0

Hydroxo species does not appear in the present system Zn^{2+} as free metal ion is present in decreasing order of its concentration with the incline in the concentration of binary complex. Maximum concentration of free metal ion Zn^{2+} is ($\approx 72\%$) which gradually decreases up to ($\approx 2\%$) in the entire pH range of 2.5-4.5.

Pb (II) –DTPA system:

Titration curves and species distribution curves in Fig. 3.2 and fig. 3.9 respectively. The species distribution curves reveal the formation of following major species: H_3L , H_2L , HL and Pb-L . The hydroxo species does not appear in the case of $\text{Pb(II)} - \text{DTPA}$ system.

The formation of binary complex takes place by the following general equation:



The species H_3L exists in the pH range 2.6 to 4.0 in the decreasing order of its concentration.

Table 3.8 and table 3.10 (ii) represent the proton-ligand formation constants of $-\text{DTPA}$ and metal ligand formation constants of Pb(II)-DTPA complex respectively.

H_2L species is also found to exist in negligible amount ($<1\%$) in the same pH range. Distribution profiles show that there is a gradual decrease in the concentration of Pb(II) as free state, which clearly indicates that Pb(II) is complexed with DTPA forming a binary complex. The formation of Pb(II)-DTPA species starts from pH 2.6 ($\approx 43\%$) and there is a gradual increase in its concentration reaching up to ($\approx 97\%$) until it becomes constant at $\text{pH} \sim 4.0$.

Be (II) –DTPA system:

Titration curves of this system are shown in fig. 3.3. The species distribution curves fig. 3.10 reveal for the formation of following species H_3L , H_2L , HL and Be -DTPA. The formation of hydroxo species of Be (II) was also taken in consideration in the calculation of formation constants. The following two hydroxo species viz, $Be(OH)^+$ & $Be(OH)_2$ were assumed and their concentrations are governed by the equilibria



Proton-Ligand formation constants of DTPA and hydrolytic constants species of Be^{2+} ion are given in table 3.8 and 3.9 respectively

The equilibrium constants of the above equations has been calculated and are given in table 3.10(iii)

$Be(OH)^+$ species appears at $pH \sim 3.5$ while $Be(OH)_2$ species shows its appearance at $pH \sim 5.0$. The concentration of both the hydroxo species increases with the rise in pH . Maximum concentration of $Be(OH)^+$ and $Be(OH)_2$ species may be identified at $pH \sim 5.75$ i.e. $\approx 40\%$ and $\approx 20\%$ respectively

It is interesting to note that in the lower pH region ($\sim 2.25-4.5$) there is a decline in the concentration of H_3L with the concomitant incline in the concentration of H_2L species. While in the higher pH region ($pH > 4.5$), the concentration of H_2L species is found to decrease with the rise in pH . The decrease in the concentration of $Be(II)$ in the same pH range also suggests the formation of binary complex $Be(II)$ –

DTPA. Thus it may be concluded that binary complexation starts beyond pH~4.25 which is governed by the equilibrium.



It is clear from the distribution diagram that the concentration of binary complex Be (II) –DTPA increases gradually with the gradual increase in pH up to ~5.5 where its concentration is maximum i.e. $\approx 90\%$

Mg (II) –DTPA system:

Titration curves Fig. 3.4 and species distribution curves Fig. 3.11 of the present system provide the existence of following general species H_3L , H_2L , and Mg (II) –L.

As is evident from the distribution profiles there is no any complex formed and 100% Mg (II) is present in free form up to pH ~ 9.0. In the pH range 1.0 –9.0 there is a gradual decrease in the concentration of H_3L species with the rise in concentration of H_2L species according to the equilibrium.



After pH~9.0 the concentration of Mg (II) in free state is found to decrease. The ligand H_2L also decreases showing coordination of Mg (II) with the ligand according to the equilibrium:



The concentration of MgL species increases with the rise in pH from 9.0 to 12.0. At pH~12.0 its concentration is maximum i.e. $\approx 65\%$

Proton-ligand formation constants of DTPA have already been given in Table-3.8. Metal-ligand formation constant of Mg(II)–DTPA system has been evaluated using SCOGS and is presented in Table-3.10 (iv)

Ca(II)– DTPA system:

In this system 1:1 metal-ligand ratio in order to binary system have been taken. The titration curves Fig. (3.5) and the species distribution curves Fig. (3.12) reveal for the formation of protonated species of the H_3L and H_2L are appeared and complex species Ca – DTPA

The formation of the binary system takes place by the following general equation



Proton ligand formation constants of DTPA and metal ligand formation constant of Ca (II) –DTPA table- 3.8 and 3.10 (v) respectively

The species H_3L (98%), H_2L (1%) predominate in the pH range 2.75 to 4.75 and 2.75 to 4.5 respectively in (1:1) system.

The species distribution curves reveals that H_3L species starts form at pH 2.75 and concentration percentage (98%) is decreases up to pH 4.75 and concentration percentage (22%) The species of H_2L is starts at

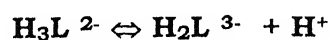
pH 2.75 and concentration percentage (1%) is also increases up to pH 4.5 and concentration percentage (80%).

The free metal ion is formed concentration percentage 100% at pH (2.75) and also constants at pH 3.5 and then decreases. The complex species range 3.5 to 5.0 and concentration percentage 60%.

Sr(II) –DTPA (1:1) system:

Titration curves and species distribution curves of the present system are given in Fig 3.6 and Fig 3.13 respectively. Proton ligand formation constants of DTPA and metal –ligand formation constants of Sr (II) -DTPA complex are given in Tables 3.8 and 3.10 (vi) respectively.

From the Fig 3.13 it is clear that with the rise in pH from 2.8 –5.0, no any Complex species appears. Almost 100% Sr(II) is present in free state. Only two types of protonated ligand species have been identified in the present system i.e. H_3L^{2-} and H_2L^{3-} . With the gradual increases in pH, the concentration of H_3L^{2-} species falls gradually, and becomes non-existent after pH~6.0. Consequently H_2L^{3-} species increases gradually, reaching maximum abundance (~90%) up to pH~5.0. Its formation is governed according to the following equilibrium:



Distribution diagram (fig.) shows that beyond pH ~ 5.0 the concentration of Sr(II) and H_2L^{3-} species decrease which may be due to complexation according to



Hence, the alkaline earth metals Sr (II) is found to coordinate with DTPA at high pH forming binary complex Sr-L in 1:1 metal to ligand ratio

Ba (II) –DTPA (1:1) system:

Fig 3.7 and Fig 3.14 shows the titration curves and distribution curves of the present binary system. Metal ligand formation constant of Ba(II) –DTPA complex has been evaluated and is given in Table 3.10 (vii). Species distribution is shown to show that Ba(II)-DTPA binary complex is formed in fairly good concentration. Its formation starts from pH 6.0 thereafter with the increase in pH from 6.0 to 8.0, its concentration is found to increase gradually attaining a maximum concentration at pH ~6.0 (~89%). Its formation takes place according to the equilibrium:

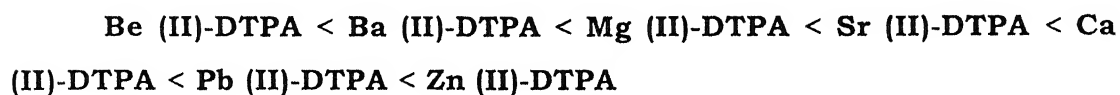


It clearly indicates the non-existence of any complex species up to pH ~ 6.0. Two types of protonated species i.e. H₃L and H₂L are remarkably present in the pH range 2.5 to 6.0 and 2.5 to 8.0 respectively. In this pH range 100% Ba(II) remains in uncomplexed free form. With the increase in pH from 2.5 to 6.0 there is a decline in the concentration of H₃L species with the concomitant incline in the concentration of H₂L species of the ligand. But beyond pH ~ 6.0 there is a gradual decrease in the concentration of H₂L species as well as of Ba(II). This indicates the process of binary complexation.

CONCLUSIVE REMARKS

The present chapter describe the formation and stability of M (II)-DTPA complexes, where M (II) = Zn (II), Pb (II), Be (II), Mg (II), Ca (II), Sr (II) and Ba (II)

Table 3 10 contains the values of stability constants of the binary complexes understudy Various reactions of the formation equilibria for the ligand have been described In general, Pb (II) –DTPA (1 1) complex has slightly higher stability than Zn(II)-DTPA complex. In case of alkaline earth metal complexes following order of stability is obtained:



It may be concluded that the binary complexes⁽¹⁹⁰⁾ with metals i.e Zn(II) and Pb (II) are formed in the low pH region while the complex with alkaline earth metals are formed only in the high pH region

It is clearly inferred from the species distribution curves Fig 3 9 to 3.15 that no hydroxo species are found to exist except in Be(II) –DTPA system where Be(OH)⁺ and Be (OH)₂ hydroxo species exist in small amounts

Table 3.1

Zn (II) – DTPA System

- A.** 5 ml NaNO_3 (1 M) + 5 ml HNO_3 (0.02 M) + 40 ml H_2O
- B.** 5 ml NaNO_3 (1 M) + 5 ml HNO_3 (0.02 M) + 5 ml DTPA (0.01 M) + 35 ml H_2O
- C.** 5 ml NaNO_3 (1 M) + 5 ml HNO_3 (0.02 M) + 5 ml DTPA (0.01 M) + 5 ml Zn (II) (0.01 M) + 25 ml H_2O

Overall strength of acid = 0.002 M HNO_3

Overall strength of Ligand = 0.001 M DTPA

Overall strength of Zn (II) = 0.001 M

Ionic Strength = 0.1 M NaNO_3

Strength of Alkali = 0.116 M NaOH

A		B		C	
Volume of NaOH ml	pH	Volume of NaOH ml	pH	Volume of NaOH ml	pH
0 00	2 64	0.00	2 79	0 00	2 37
0 20	2 75	0.20	2.90	0 20	2.42
0 40	2 88	0.40	3 03	0 40	2 46
0 60	3 05	0.60	3 22	0 60	2 50
0 80	4.15	0 80	3 46	0 80	2 61
1 00	9.80	1.00	3 80	1 00	2.69
1 20	10 23	1.20	4.35	1 20	2 78
1 40	10 43	1.40	5 39	1.40	2.88
1.60	10.56	1 60	8 01	1 60	2 97
1 80	10 67	1 80	8 66	1 80	3.13
2 00	10 75	2 00	9 22	2 00	3 35
2 20	10 81	2 20	9 67	2 20	3 63
2 40	10 87	2 40	10 00	2 40	4 28
2 60	10 92	2 60	10.24	2 60	5 21
2 80	10.97	2.80	10 43	2.80	6 43
3 00	11 01	3 00	10 57	3 00	8.51
3 20		3 20	10 67	3 20	8.94
3 40		3 40	1076	3.40	9 67
3 60		3 60	10 83	3 60	10.20
3 80		3.80	10.89	3 80	10.44
4.00		4.00	10 95	4 00	10.57
4 20		4 20	11 00	4.20	10 71
4 40		4.40	11 04	4.40	

Table 3.2

Pb(II) -DTPA System

- A.** 5 ml NaNO_3 (1 M) + 5 ml HNO_3 (0.02 M) + 40 ml H_2O
- B.** 5 ml NaNO_3 (1 M) + 5 ml HNO_3 (0.02 M) + 5 ml DTPA (0.01 M) + 35 ml H_2O
- C.** 5 ml NaNO_3 (1 M) + 5 ml HNO_3 (0.02 M) + 5 ml DTPA (0.01 M) + 5 ml Pb (II) (0.01 M) + 30 ml H_2O

Overall strength of acid = 0.002 M HNO_3

Overall strength of Ligand = 0.001 M DTPA

Overall strength of Pb(II) = 0.001 M

Ionic Strength = 0.1 M NaNO_3

Strength of Alkali = 0.116 M NaOH

A		B		C	
Volume of NaOH ml	pH	Volume of NaOH ml	pH	Volume of NaOH ml	pH
0 00	2 64	0.00	2 79	0 00	2 56
0.20	2.75	0 20	2 90	0 20	2 60
0.40	2 88	0 40	3 03	0.40	2.65
0.60	3 05	0 60	3 22	0.60	2 67
0 80	4 15	0 80	3 46	0 80	2.71
1.00	9 80	1.00	3 80	1 00	2 76
1 20	10 23	1 20	4.35	1 20	2.81
1 40	10.43	1.40	5.39	1.40	2 89
1.60	10.56	1 60	8.01	1.60	2.97
1 80	10 67	1 80	8.66	1.80	3 10
2.00	10 75	2 00	9.22	2.00	3.20
2.20	10 81	2.20	9.67	2.20	3.35
2 40	10 87	2 40	10 00	2.40	3 57
2 60	10 92	2 60	10 24	2.60	3 92
2 80	10 97	2 80	10.43	2 80	432
3 00	11 01	3 00	10.57	3.00	4 78
3 20		3.20	10 67	3.20	5 65
3 40		3.40	1076	3.40	9.47
3 60		3.60	10.83	3 60	10.19
3 80		3.80	10 89	3 80	10 48
4 00		4.00	10 95	4.00	10 62
4 20		4.20	11.00	4.20	1075
4 40		4.40	11 04	4.40	10.83

Table 3.3

Be (II) – DTPA System

- A.** 5 ml NaNO_3 (1 M) + 5 ml HNO_3 (0.02 M) + 40 ml H_2O
- B.** 5 ml NaNO_3 (1 M) + 5 ml HNO_3 (0.02 M) + 5 ml DTPA (0.01 M) + 35 ml H_2O
- C.** 5 ml NaNO_3 (1 M) + 5 ml HNO_3 (0.02 M) + 5 ml DTPA (0.01 M) + 5 ml Be (II) (0.01 M) + 30 ml H_2O

Overall strength of acid = 0.002 M HNO_3

Overall strength of Ligand = 0.001 M DTPA

Overall strength of Be (II) = 0.001 M

Ionic Strength = 0.1 M NaNO_3

Strength of Alkali = 0.116 M NaOH

A		B		C	
Volume of NaOH ml	pH	Volume of NaOH ml	pH	Volume of NaOH ml	pH
0.00	2.64	0.00	2.79	0.00	2.77
0.20	2.75	0.20	2.90	0.20	2.87
0.40	2.88	0.40	3.03	0.40	2.98
0.60	3.05	0.60	3.22	0.60	3.12
0.80	4.15	0.80	3.46	0.80	3.31
1.00	9.80	1.00	3.80	1.00	3.56
1.20	10.23	1.20	4.35	1.20	3.85
1.40	10.43	1.40	5.39	1.40	4.14
1.60	10.56	1.60	8.01	1.60	4.43
1.80	10.67	1.80	8.66	1.80	4.72
2.00	10.75	2.00	9.22	2.00	5.07
2.20	10.81	2.20	9.67	2.20	5.70
2.40	10.87	2.40	10.00	2.40	6.22
2.60	10.92	2.60	10.24	2.60	6.51
2.80	10.97	2.80	10.43	2.80	7.35
3.00	11.01	3.00	10.57	3.00	8.25
3.20		3.20	10.67	3.20	8.86
3.40		3.40	10.76	3.40	9.36
3.60		3.60	10.83	3.60	9.72
3.80		3.80	10.89	3.80	10.02
4.00		4.00	10.95	4.00	10.23
4.20		4.20	11.00	4.20	10.40
4.40		4.40	11.04	4.40	10.54

Table 3.4

Mg(II) – DTPA System

- A.** 5 ml NaNO_3 (1 M) + 5 ml HNO_3 (0.02 M) + 40 ml H_2O
- B.** 5 ml NaNO_3 (1 M) + 5 ml HNO_3 (0.02 M) + 5 ml DTPA (0.01 M) + 35 ml H_2O
- C.** 5 ml NaNO_3 (1 M) + 5 ml HNO_3 (0.02 M) + 5 ml DTPA (0.01 M) + 5 ml Mg(II) (0.01 M) + 30 ml H_2O

Overall strength of acid = 0.002 M HNO_3

Overall strength of Ligand = 0.001 M DTPA

Overall strength of Mg (II) = 0.001 M

Ionic Strength = 0.1 M NaNO_3

Strength of Alkali = 0.116 M NaOH

A Acid		B DTPA		C Mg-DTPA	
Volume of NaOH ml	pH	Volume of NaOH ml	pH	Volume of NaOH ml	pH
0 00	2 64	0 00	2 79	0 00	2 85
0 20	2 75	0 20	2 90	0.20	2 95
0 40	2 88	0 40	3.03	0.40	3.07
0.60	3 05	0.60	3.22	0 60	3.23
0 80	4 15	0 80	3.46	0 80	3.47
1 00	9 80	1 00	3 80	1 00	3 79
1 20	10 23	1.20	4.35	1.20	4 16
1 40	10 43	1 40	5.39	1.40	4 59
1 60	10 56	1.60	8 01	1.60	5 02
1 80	10 67	1 80	8.66	1.80	5 56
2.00	10 75	2.00	9 22	2.00	6 15
2.20	10 81	2.20	9 67	2.20	6 68
2 40	10 87	2.40	10.00	2 40	7 11
2 60	10.92	2.60	10.24	2.60	7.73
2.80	10.97	2.80	10 43	2 80	8.99
3 00	11 01	3.00	10 57	3 00	9 88
3 20		3 20	10 67	3 20	10.27
3 40		3.40	1076	3 40	10.48
3 60		3.60	10 83	3.60	10 61
3 80		3.80	10 89	3.80	10 72
4 00		4 00	10 95	4.00	10 80
4 20		4.20	11 00	4 20	10 87
4.40		4.40	11.04	4.40	10.93

Table 3.5

Ca (II) – DTPA System

- A.** 5 ml NaNO_3 (1 M) + 5 ml HNO_3 (0.02 M) + 40 ml H_2O
- B.** 5 ml NaNO_3 (1 M) + 5 ml HNO_3 (0.02 M) + 5 ml DTPA (0.01 M) + 35 ml H_2O
- C.** 5 ml NaNO_3 (1 M) + 5 ml HNO_3 (0.02 M) + 5 ml DTPA (0.01 M) + 5 ml Ca(II) (0.01 M) + 30 ml H_2O

Overall strength of acid = 0.002 M HNO_3

Overall strength of Ligand = 0.001 M DTPA

Overall strength of Ca (II) = 0.001 M

Ionic Strength = 0.1 M NaNO_3

Strength of Alkali = 0.116 M NaOH

A		B		C	
Volume of NaOH ml	pH	Volume of NaOH ml	pH	Volume of NaOH ml	pH
0 00	2.64	0.00	2 79	0 00	2 66
0.20	2.75	0 20	2 90	0 20	2 74
0 40	2 88	0.40	3 03	0 40	2 82
0 60	3 05	0 60	3 22	0.60	2 93
0 80	4 15	0.80	3 46	0.80	3 08
1 00	9.80	1 00	3.80	1 00	3.36
1 20	10.23	1 20	4 35	1.20	4.71
1 40	10.43	1 40	5.39	1.40	9.87
1 60	10 56	1.60	8.01	1.60	10 32
1 80	10 67	1 80	8 66	1.80	10 54
2 00	10 75	2.00	9.22	2.00	10 69
2 20	10.81	2.20	9.67	2.20	10 82
2 40	10 87	2 40	10.00	2 40	10 92
2 60	10 92	2.60	10 24	2.60	11 00
2 80	10 97	2 80	10.43	2 80	11 06
3.00	11 01	3.00	10 57	3.00	11.12
3 20		3 20	10 67	3.20	11.17
3 40		3.40	1076	3.40	11.21
3 60		3.60	10.83	3.60	11.26
3.80		3.80	10.89	3.80	11.88
4 00		4 00	10 95	4.00	
4 20		4.20	11.00	4.20	
4 40		4 40	11.04	4.40	

Table 3.6

Sr (II) – DTPA System

- A.** 5 ml NaNO_3 (1 M) + 5 ml HNO_3 (0.02 M) + 40 ml H_2O
- B.** 5 ml NaNO_3 (1 M) + 5 ml HNO_3 (0.02 M) + 5 ml DTPA (0.01 M) + 35 ml H_2O
- C.** 5 ml NaNO_3 (1 M) + 5 ml HNO_3 (0.02 M) + 5 ml DTPA (0.01 M) + 5 ml Sr(II) (0.01 M) + 30 ml H_2O

Overall strength of acid	= 0.002 M HNO_3
Overall strength of Ligand	= 0.001 M DTPA
Overall strength of Sr(II)	= 0.001 M
Ionic Strength	= 0.1 M NaNO_3
Strength of Alkali	= 0.116 M NaOH

A		B		C	
Volume of NaOH ml	pH	Volume of NaOH ml	pH	Volume of NaOH ml	pH
0 00	2 64	0 00	2 79	0.00	2 80
0 20	2 75	0 20	2 90	0.20	2 89
0 40	2 88	0 40	3.03	0 40	3 01
0 60	3.05	0 60	3 22	0 60	3 17
0 80	4.15	0 80	3.46	0 80	3 38
1.00	9.80	1 00	3.80	1 00	3 65
1 20	10.23	1 20	4.35	1 20	4 00
1 40	10 43	1 40	5 39	1 40	4 38
1 60	10 56	1 60	8.01	1 60	5 06
1.80	10.67	1 80	8.66	1 80	5.77
2.00	10 75	2 00	9 22	2 00	6 10
2 20	10 81	2 20	9.67	2 20	6 37
2 40	10 87	2 40	10 00	2 40	6.76
2 60	10 92	2 60	10 24	2 60	6 60
2 80	10 97	2 80	10 43	2.80	9 34
3 00	11 01	3.00	10 57	3.00	9.98
3 20		3.20	10 67	3 20	10.30
3 40		3 40	1076	3 40	10 49
3 60		3 60	10 83	3.60	10 61
3 80		3 80	10.89	3 80	10 71
4 00		4 00	10.95	4.00	10 79
4 20		4 20	11.00	4.20	10 85
4.40		4.40	11.04	4.40	10.91

Table 3.7

Ba(II) – DTPA System

A. 5 ml NaNO_3 (1 M) + 5 ml HNO_3 (0.02 M) + 40 ml H_2O

B. 5 ml NaNO_3 (1 M) + 5 ml HNO_3 (0.02 M) + 5 ml DTPA (0.01 M) + 35 ml H_2O

C. 5 ml NaNO_3 (1 M) + 5 ml HNO_3 (0.02 M) + 5 ml DTPA (0.01 M) + 2ml Ba (II) (0.01 M) + 30 ml H_2O

Overall strength of acid = 0.002 M HNO_3

Overall strength of Ligand = 0.001 M DTPA

Overall strength of Ba (II) = 0.001 M

Ionic Strength = 0.1 M NaNO_3

Strength of Alkali = 0.116 M NaOH

A		B		C	
Volume of NaOH ml	pH	Volume of NaOH ml	pH	Volume of NaOH ml	pH
0 00	2 64	0 00	2 79	0.00	2 74
0 20	2 75	0 20	2 90	0 20	2.82
0 40	2 88	0 40	3 03	0 40	2.90
0 60	3 05	0 60	3 22	0.60	3 01
0 80	4 15	0 80	3.46	0.80	3 16
1 00	9 80	1.00	3.80	1.00	3 37
1 20	10 23	1 20	4 35	1.20	3 68
1 40	10 43	1 40	5 39	1.40	4.13
1 60	10 56	1 60	8 01	1 60	5 03
1 80	10 67	1 80	8 66	1 80	6 20
2 00	10 75	2 00	9 22	2 00	6.61
2 20	10 81	2 20	9 67	2.20	6 90
2.40	10.87	2 40	10 00	2 40	7 32
2 60	10.92	2.60	10 24	2.60	9 01
2.80	10.97	2 80	10 43	2.80	10 15
3 00	11.01	3 00	10.57	3.00	10 46
3 20		3 20	10 67	3.20	10.63
3 40		3 40	1076	3.40	10 75
3.60		3 60	10 83	3.60	10.87
3.80		3 80	10 89	3.80	10.94
4 00		4.00	10 95	4.00	11.01
4.20		4.20	11 00	4.20	11.07
4.40		4.40	11 04	4.40	11.13

Table 3.8

Proton –Ligand formation constant ($\log \beta_{\text{overall}}$) of DTPA at $\pm 37 \text{ }^{\circ}\text{C}$ and $\mu=0.1 \text{ mole dm}^{-3} \text{ NaNO}_3$.

S NO	Species	p	q	r	s	t	$\log \beta$
(i)	H_5L	0	0	1	0	-5	27.68
(ii)	H_4L	0	0	1	0	-4	25.86
(iii)	H_3L	0	0	1	0	-3	23.21
(iv)	H_2L	0	0	1	0	-2	18.98
(v)	HL	0	0	1	0	-1	10.45

Table 3.9

Hydrolytic constants of Be^{2+} aq. ion

S NO	Species	p	q	r	s	t	$\log \beta$
(i)	Be (OH)^+	1	0	0	0	1	-5.70
(ii)	Be (OH)_2	1	0	0	0	2	-11.16

Table 3.10

Metal –Ligand formation constant :Binary system

S NO	Species	p	q	r	s	t	log β
(i)	Zn (II)-DTPA	1	0	1	0	0	18.22
(ii)	Pb(II)-DTPA	1	0	1	0	0	18.58
(iii)	Be (II)-DTPA	1	0	1	0	0	8.53
(iv)	Mg (II)-DTPA	1	0	1	0	0	9.28
(v)	Ca (II)-DTPA	1	0	1	0	0	10.69
(vi)	Sr (II)-DTPA	1	0	1	0	0	9.67
(vii)	Ba (II)-DTPA	1	0	1	0	0	8.73

Table 3.11

Stability constant values for the metal-ligand (1:1) complexes binary system	
Reaction (metal- ligand (1:1))	log β
$\text{Zn}^{2+} + \text{DTPA}^{5-} \rightleftharpoons [\text{Zn- DTPA-Zn}]^{-}$	18.22
$\text{Pb}^{2+} + \text{DTPA}^{5-} \rightleftharpoons [\text{Pb- DTPA-Pb}]^{-}$	18.58
$\text{Be}^{2+} + \text{DTPA}^{5-} \rightleftharpoons [\text{Be- DTPA-Be}]^{-}$	8.53
$\text{Mg}^{2+} + \text{DTPA}^{5-} \rightleftharpoons [\text{Mg- DTPA-Mg}]^{-}$	9.28
$\text{Ca}^{2+} + \text{DTPA}^{5-} \rightleftharpoons [\text{Ca- DTPA-Ca}]^{-}$	10.69
$\text{Sr}^{2+} + \text{DTPA}^{5-} \rightleftharpoons [\text{Sr- DTPA-Sr}]^{-}$	9.67
$\text{Ba}^{2+} + \text{DTPA}^{5-} \rightleftharpoons [\text{Ba- DTPA-Ba}]^{-}$	8.73

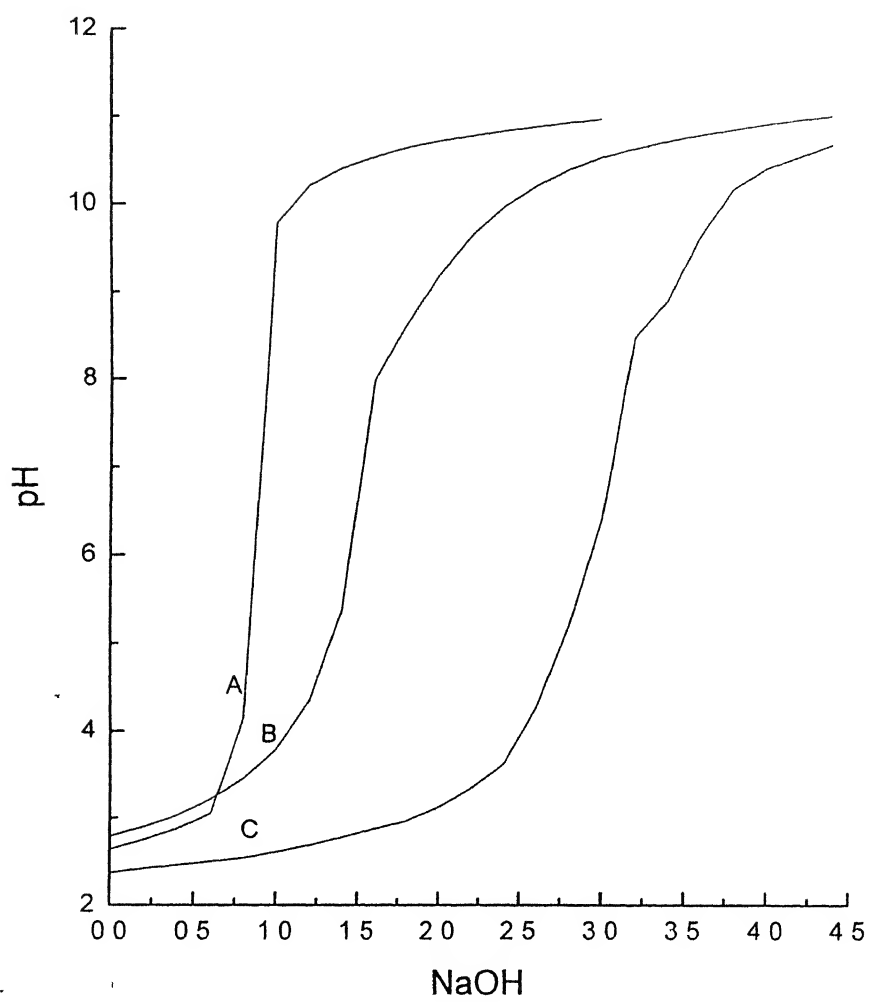


Fig 3 1 Titration curves of Zn(II)-DTPA System

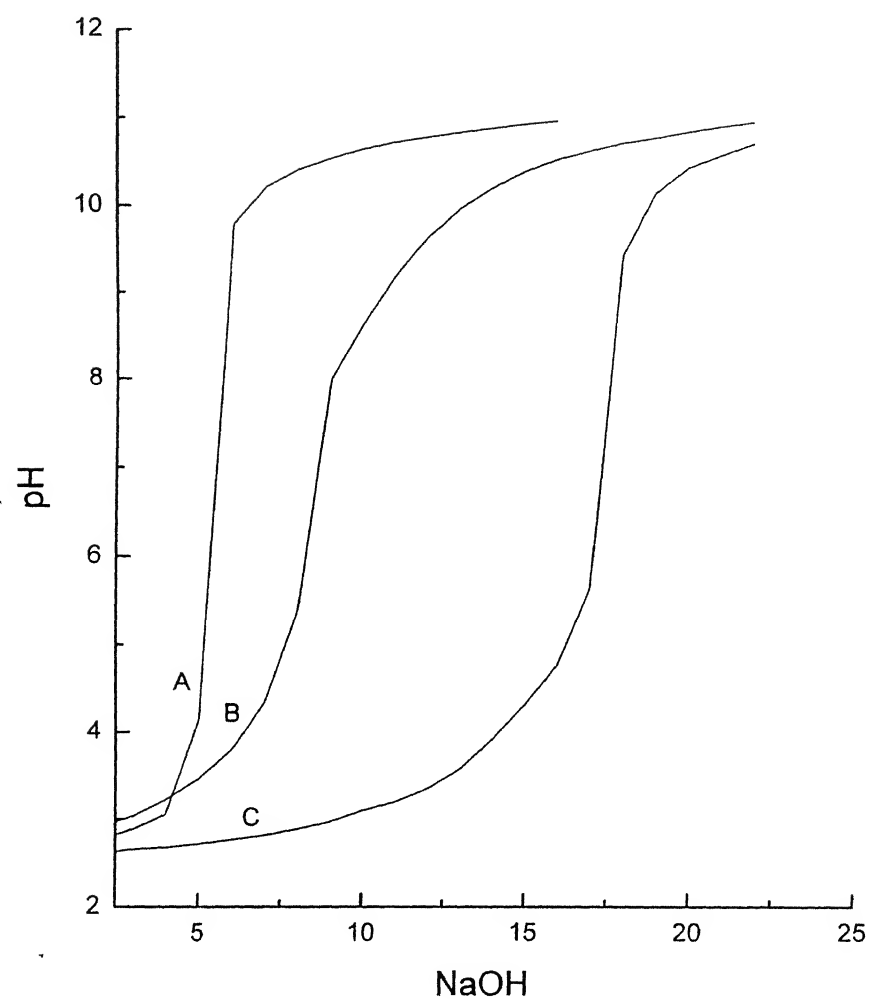


Fig. 3.2 Titration curves of Pb(II)-DTPA System.

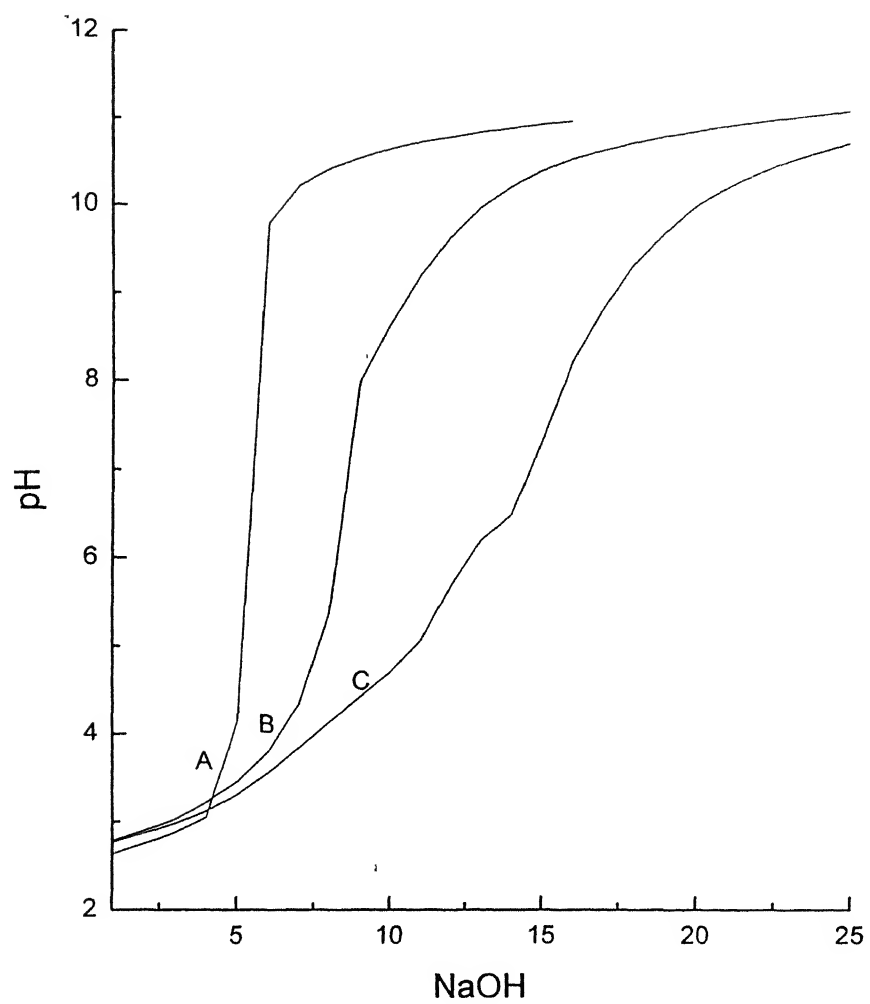


Fig. 3.3 Titration curves of Be(II)-DTPA System.

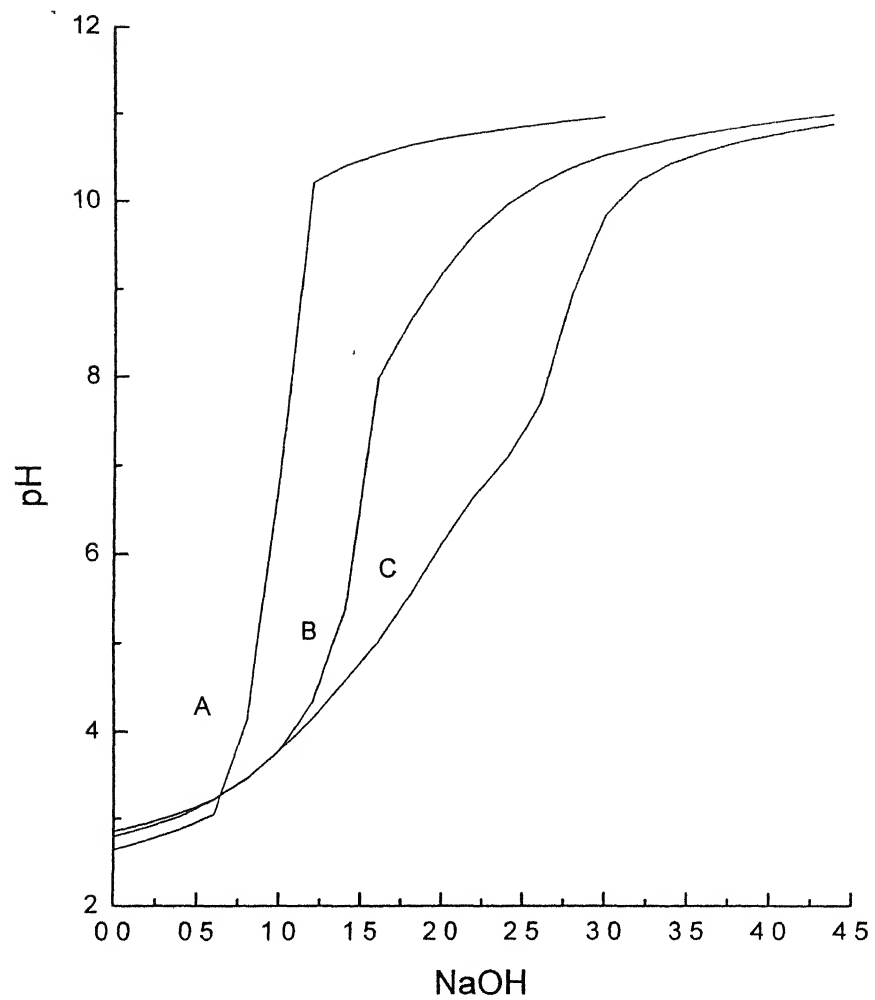


Fig. 3.4 Titration curves of Mg(II)-DTPA System.

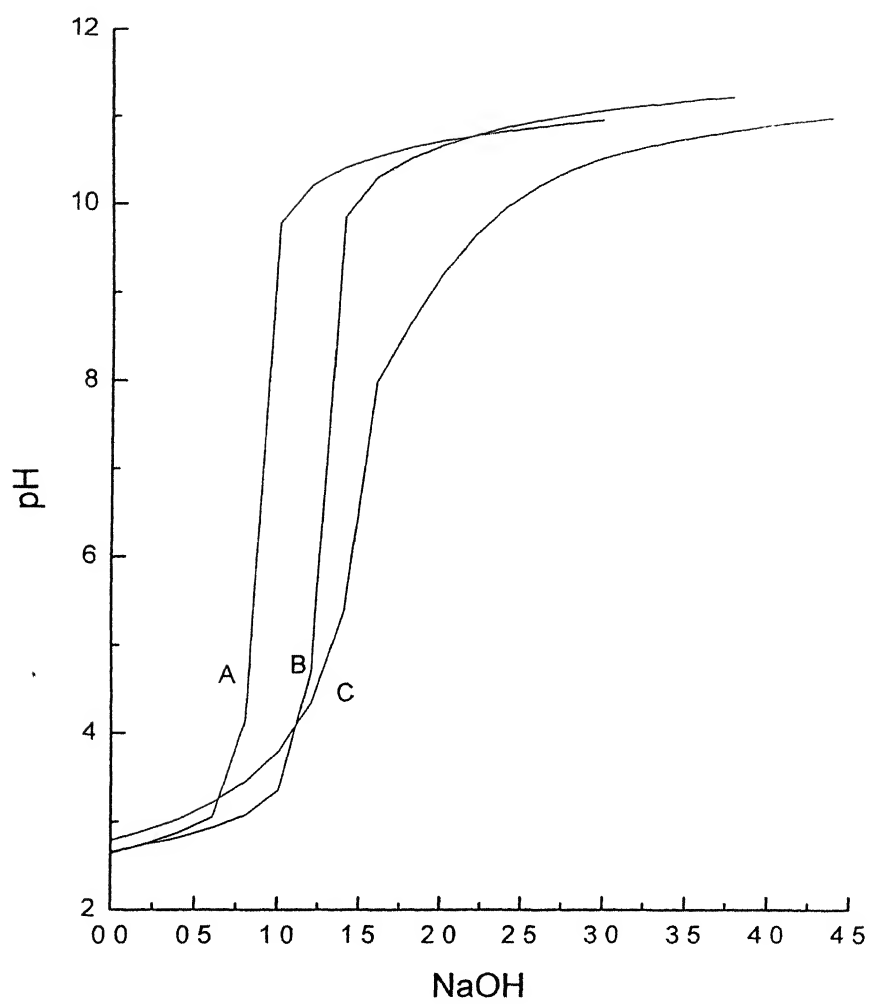


Fig. 3.5 Titration curves of Ca(II)-DTPA System.

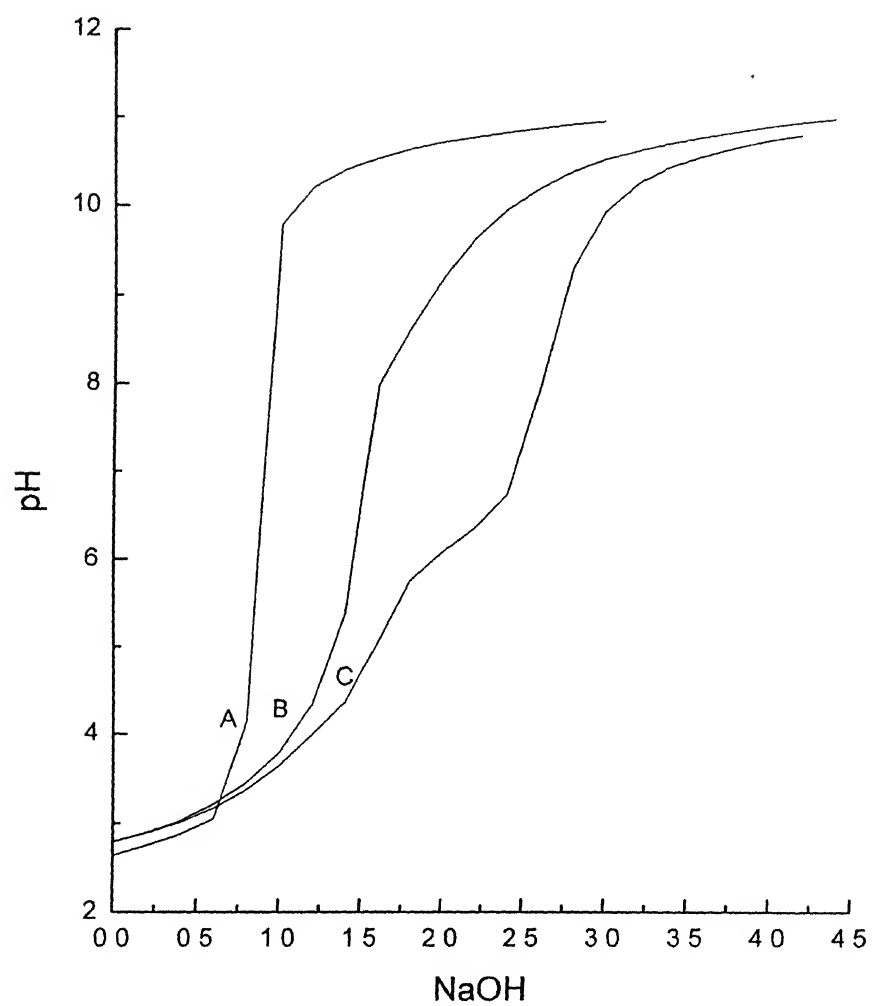


Fig. 3.6 Titration curves of Sr(II)-DTPA System.

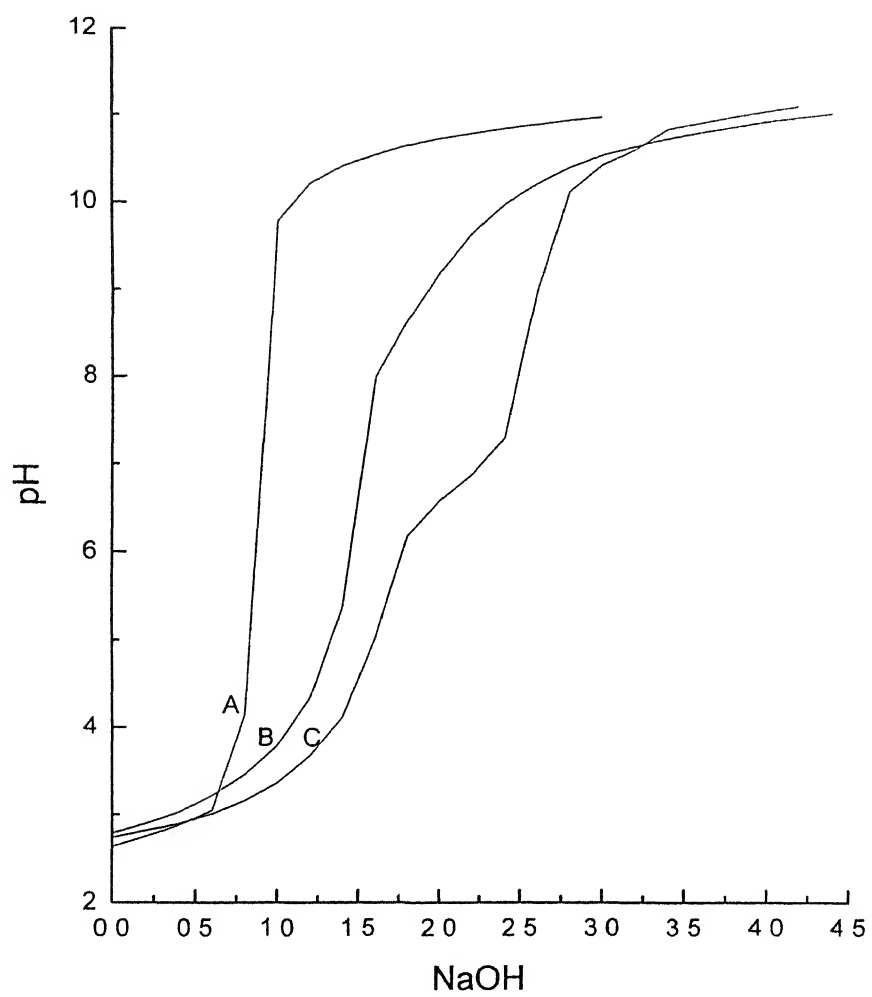


Fig. 3.7 Titration curves of Ba(II)-DTPA System.

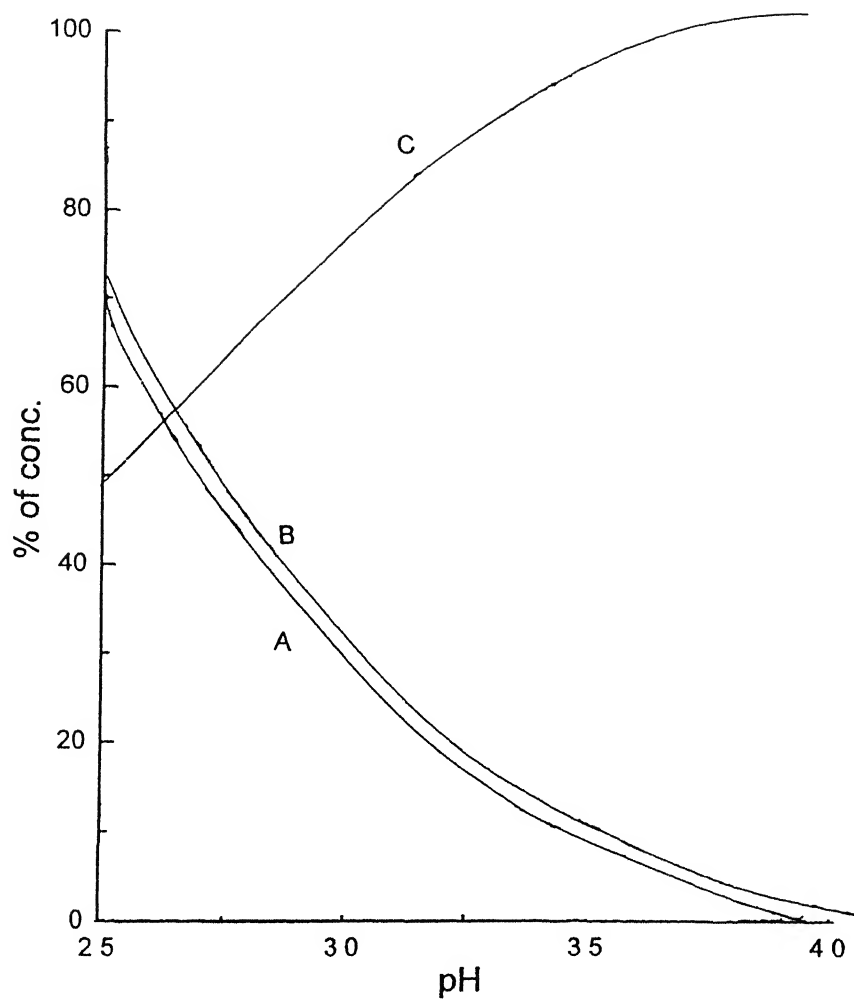


Fig 3.8. Species distribution curve of Zn(II)-DTPA System
Where (A) H₃L (B) ZnH₂L⁺ (C) Zn(II)-DTPA

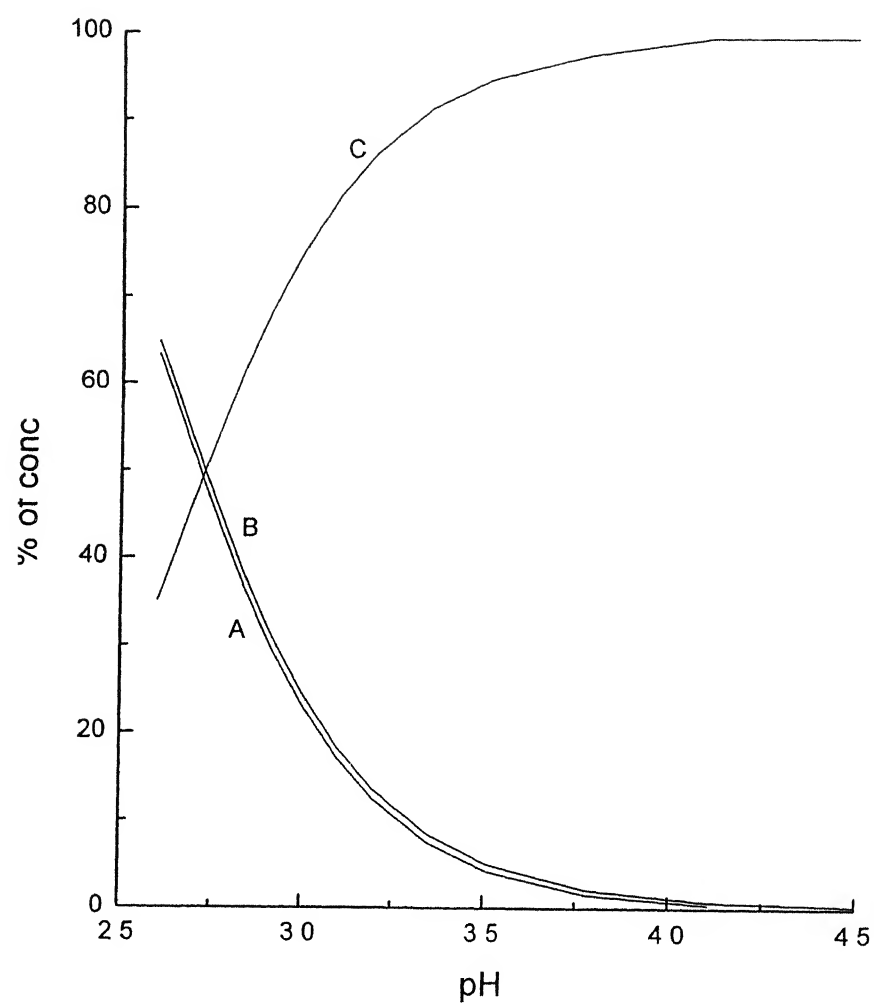


Fig. 3 9 Species distribution curve of Pb(II) DTPA System where (A) H₃L (B) Pb(II) (C) Pb(II)- DTPA

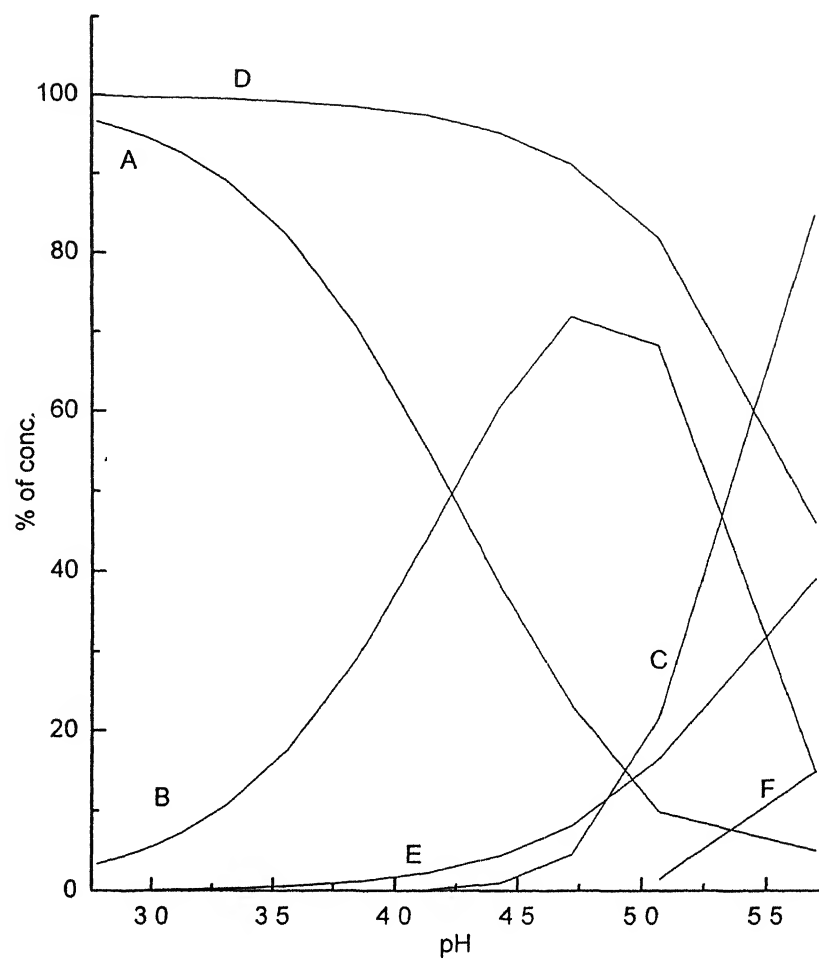


Fig 3 10 Species distribution curve of Be(II)-DTPA System
Where (A) H_3L (B) H_2L (C) Be(II)-DTPA (D) Be(II) (E) $Be(OH)^+$
(F) $Be(OH)_2$

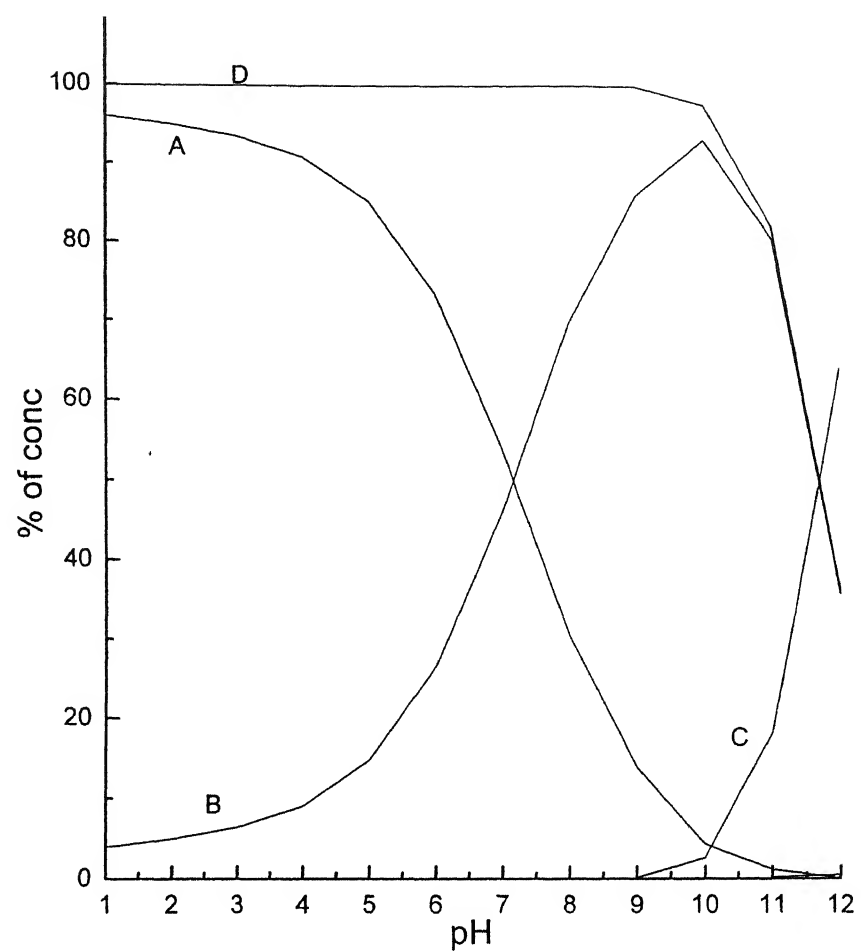


Fig 3 11 Species distribution curve of Mg(II)-DTPA System
Where (A) H_3L (B) H_2L (C) Mg(II)-DTPA (D) Mg(II)

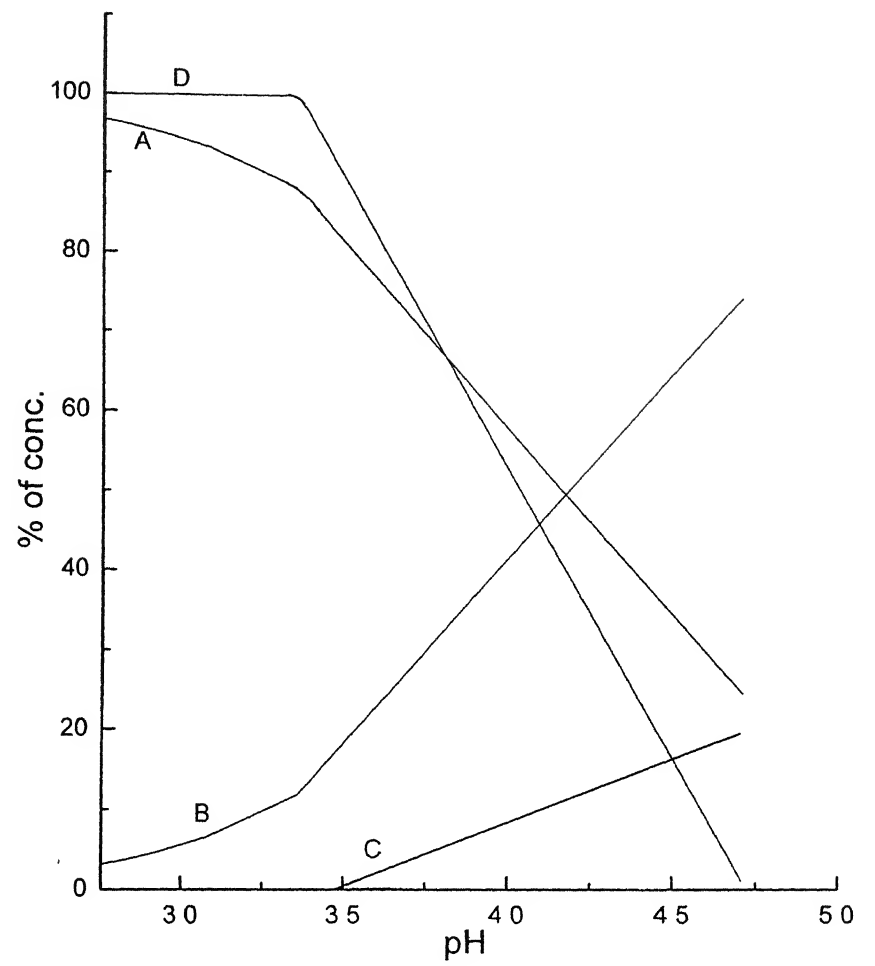


Fig 3 12 Species distribution curve of $Ca(II)$ -DTPA System
Where (A) H_3L (B) H_2L (C) $Ca(II)$ -DTPA (D) $Ca(II)$

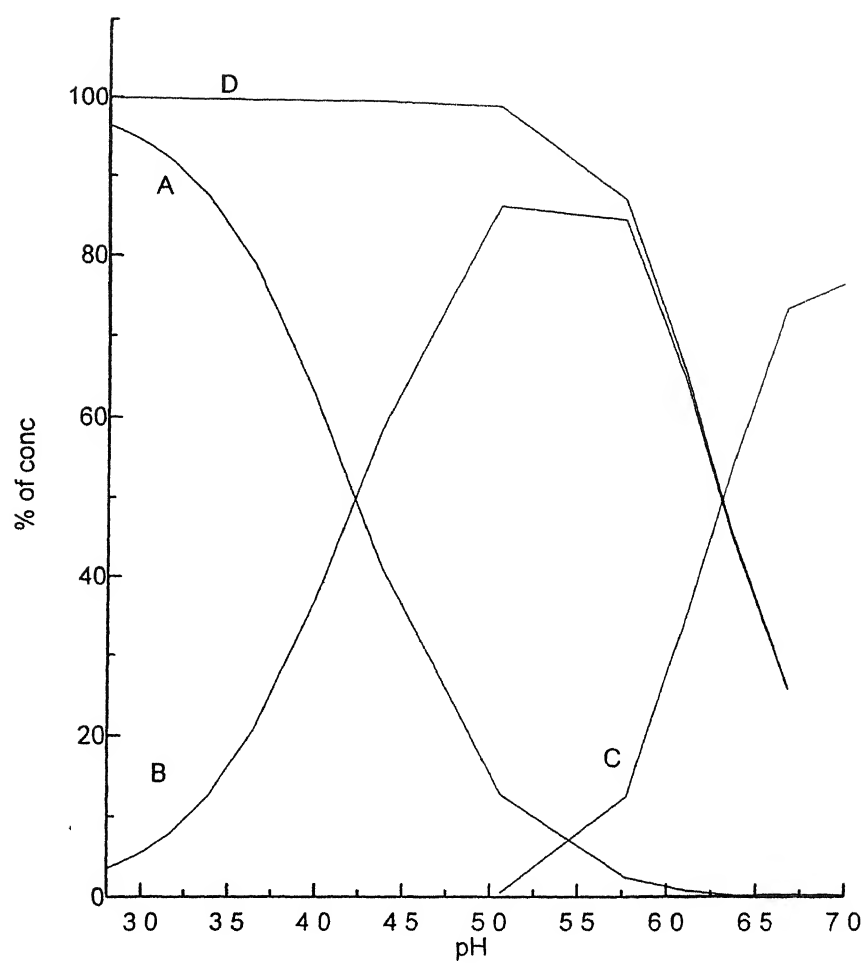


Fig 3.13 Species distribution curve of Sr(II)-DTPA (1:1) System
Where (A) H₃L (B) H₂L (C) Sr(II)-DTPA (D) Sr(II)

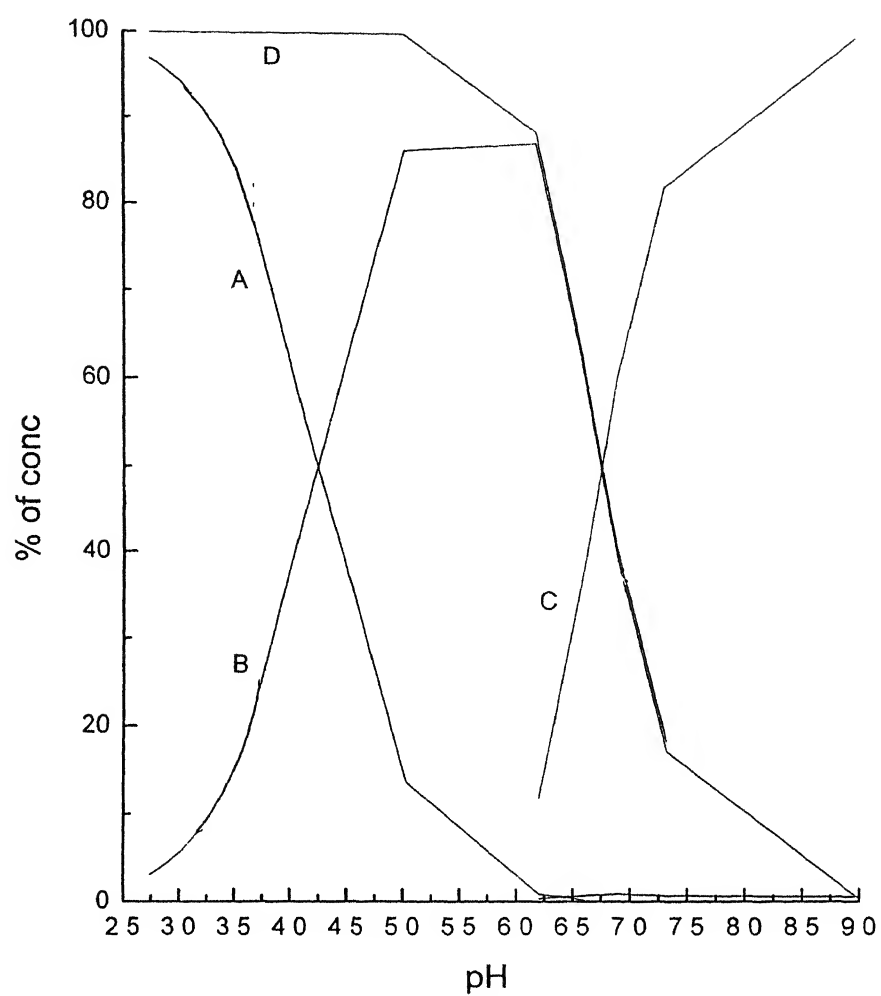


Fig 3 14 Species distribution curve of Ba(II)-DTPA System
Where (A) H_3L (B) H_2L (C) $Ba(II)$ -DTPA (D) $Ba(II)$

CHAPTER IV

FORMATION EQUILIBRIA OF HOMOBIMETALLIC SYSTEMS

The present chapter deals with the homobimetallic⁽¹⁹¹⁾ complexes formed by Diethylenetriaminepentaacetic acid (DTPA) with Zn (II), Pb(II), Be(II), Mg(II), Sr (II) and Ba(II) system in aqueous medium at $37 \pm 1^\circ$ and $\mu = 0.1 \text{ mol dm}^{-3} \text{ NaNO}_3$. The relevant stability constants have been evaluated using SCOGS computer program.

Titration Procedure:

These reaction mixtures were prepared by keeping the total volume 50 ml in each case and the molar ratio of ligand and metals undertaken was kept 2 : 1.

Solution A: 10 ml NaNO_3 (1 mol dm^{-3}) + 10 ml HNO_3 (0.02 mol dm^{-3}) + 40 ml H_2O

Solution B: 5 ml NaNO_3 (1 mol dm^{-3}) + 5 ml DTPA (1 mol dm^{-3}) + 35 ml H_2O

Solution C: 5 ml NaNO_3 (1 mol dm^{-3}) + 5 ml HNO_3 (0.02 mol dm^{-3}) + 5 ml DTPA (1 mol dm^{-3}) + 10 ml M (II) (0.1 mol dm^{-3}) + 25 ml H_2O

Where, M (II) is the metal ion of the various system mentioned above.

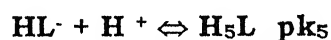
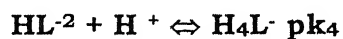
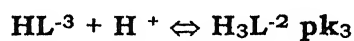
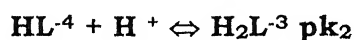
The Table 4.1 to 4.6 and the titration curves are shown in Figures 4.1 to 4.6. The plot of pH against the volume of alkali gives the titration curves A, B & C to acid, DTPA and M (II)–DTPA complex respectively.

SPECIES DISTRIBUTION CURVES:

The plot of % concentration against pH gives the distribution curves of the species formed. These distribution curves are obtained by running the computer program ORIGIN 4.0 and are shown in Fig. 4.7 to 4.12. The distribution of binary system has been sketched and studied in

order to explain the comparative chelating behavior of the ligand towards both the metal ions under study

The proton- ligand formation constants of DTPA determined by Irving- Rossotti titration technique are given in Table 4 7 DTPA shows five replicable protons The proton –ligand formation constants reported in agree with the literature values Due to the presence of five coarboxylic groups, it behaves as penta basic acid Its protonation equilibria are expressed as



Metal–ligand formation constants:

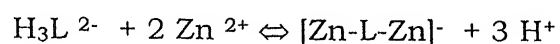
The Table 4 9 represents the refined values of binary and hydroxo species of M (II)–DTPA system taken understudy

The computer gives the values of the constants ($\log \beta_{pqrst}$) and also the concentration distribution of the complex species at different pH values as the output described further.

Zn (II) DTPA (2:1) System:

The titration curves and species distribution curves Fig 4 7 of the present system clearly indicate the formation of homobimetallic complex⁽¹⁹²⁾ Zn (II)-DTPA-Zn (II) in the pH range ~3.0-5.6. There is a gradual increase in the concentration of complex with the gradual increase in pH reaching a maximum concentration at pH ~5.6 i.e. ~75%

Besides the complex Zn (II)-DTPA-Zn (II), H₃L, H₂L species of the ligand and Zn (II) in the free form are also identifiable. Both H₃L and Zn (II) species are present in the decreasing of their concentrations which indicates their involvement in binary complexation as per equilibrium



H₂L species of the ligand is present in negligible amount. Protonated species (Table 4 7) H₃L is nearly 100% at pH ~ 2.6 while after a gradual decrease drops to negligible at pH ~ 5.0. Similarly Zn (II) in free state is ~ 100% at pH ~ 2.5 while its concentration falls gradually reaching up to negligible at pH ~5.5

The metal ligand formation constant of metal to ligand complex in 2 : 1 ratio has been calculated using SCOGS and is given in Table 4 9 (1)

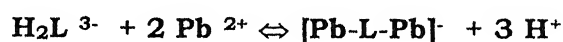
Pb (II) DTPA (2:1) System:

In the present system 2 : 1 Pb (II) to ligand ratio has been taken. The titration curves of this system are given in Fig. 4 2 and the species distribution curves Fig. 4.8 show the existence of following species H₃L, H₂L, Pb (II) and Pb (II)-L-Pb (II).

Protonated species (Table 4 7) of the ligand i.e. H₃L is nearly 100% at the beginning of the titration. But with the gradual addition of alkali, there is a gradual decrease in its concentration at pH~4.5 its concentration is negligible. Another protonated species of the ligand viz

H₂L at first increases upto pH 4.0 (≈ 15%) and then decreases attaining a minimum concentration (<1%) at pH~5.5

Pb(II) is present in uncomplexed form at pH~2.6 and with the rise in pH due to complexation, its concentration decreases gradually. At pH ~5.5 it is present in negligible amount. Following equilibria are assumed to operate in the present system.

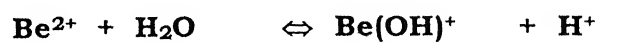


Metal ligand formation constant of the present homobimetallic complex has been given in Table 4.9 (ii)

Be (II)-DTPA (2:1) System:

The titration curves (Table 4.3) and the species distribution curves Fig. 4.9 reveal for the formation of following major species: H₃L, H₂L, HL of Be (II) –DTPA- Be (II). The proton – ligand formation constants of the present homobimetallic complex has been given in Table 4.7

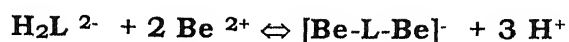
The formation of hydroxo complex of Be (II) was also taken in consideration in the calculation of formation constants. It is shown in Table 4.8. The following hydroxo species viz; Be (OH)⁺ & Be (OH)₂ were assumed and their concentrations are governed by the equilibria.



The equilibrium constants of the above equations have been calculated and are given in Table 4.9 (iii). The hydroxo species are not

clearly seen in the species distribution curves (owing to their percentage less than 1%)

The formation of binary complex takes place by the following general equation



The species distribution curves reveal that the formation Be(II) – DTPA – Be(II)

Starts from pH~6.25 and there is a gradual increase in its concentration reaching up to 35% at pH~7.5

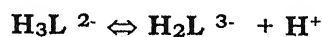
Be (II) as free metal ion is present in decreasing order of its concentration at pH > 6.25 with the incline in the concentration of binary complexes. Maximum concentration of free metal ion Be (II) is (100%) in the pH range 2.5 to 6.25 which gradually decreases up to 45 % in the pH range 6.25 to 7.5

Mg (II)-DTPA (2:1) System:

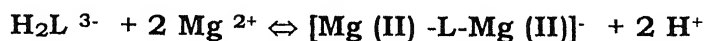
Fig 4.4 and Fig 4.10 represent the titration curves and species distribution curves of Mg (II)-DTPA system respectively. Metal to ligand ratio has been taken as 2:1. Metal ligand formation constant of this homobimetallic binary system is given in Table 4.9 (iv)

H₃L and H₂L are the two types of protonated ligand species (Table 4.7) showing their marked presence from pH ~3.0 to 6.5. Speciation curves show that with the increase in pH, there is gradual fall in the concentration of H₃L species with the concomitant incline in the

concentration H_2L species. At pH~6.5 H_3L species is negligible while H_2L the equilibria governing the concentration distribution of these species are following



Mg (II) in free state remains almost constant (100%) in the entire low pH region. But beyond pH~6.5, the binary complex is formed with the simultaneous coordination of Mg (II) and H_2L species in 2:1 ratio according to the equilibrium

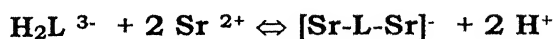


Rise in the concentration of binary complex is accompanied by fall in the concentration of Mg (II) and H_2L species.

Sr (II)-DTPA (2:1) System:

Titration curves and speciation curves of the present binary system are given in Fig 4.5 and Fig 4.11 respectively

Both the figures clearly indicate that binary complex in 2:1 metal to ligand ratio is forming after pH ~ 6.2. Its concentration gradually increases with the increase in pH reaching a maximum concentration (~28%) at pH ~8.0. In the low pH region i.e. 3.0-6.0 no complexation occurs. Fall in the concentration of H_3L species is accompanied by rise in the concentration of H_2L species and at pH ~6.2, the concentrations of H_3L and H_2L species are ~<1% and ~99% respectively.

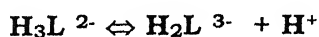


100% Sr(II) is present in free form in the pH range ~3.0-6.0 and beyond this pH its concentration falls due to its coordination with the ligand, homobimetallic (Sr (II) -L-Sr (II)) complex starts forming from pH~6.2 where its concentration is negligible and exceeds up to 40% at pH ~8.0. The Metal - ligand formation constants of the present homobimetallic complex have been given in table 4.9(v)

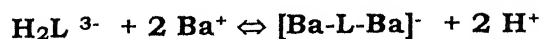
Ba (II)-DTPA (2:1) System:

Similar to other alkaline earth metals Ba (II) also coordinates with the ligand at high pH region. Species distribution curves Fig 4.12 clearly show that in the low pH region Ba(II) in uncomplexed form remains constant (~100%) up to pH~6.0 and beyond this pH its concentration decreases.

H₃L species of the ligand is nearly 90% at pH~ 3.0, which gradually decreases with the increase in pH. Consequently H₂L species originates which after a gradual increase attains a maximum concentration at pH~6.0. At this pH the concentration of H₃L species is almost negligible.



It is clear from the speciation curves that after pH~6.0 the concentration of Ba(II) and of H₂L species are decreasing and on the other hand this decrease is followed by an increase in the concentration of binary complex according to the equilibrium



Maximum concentration of this homobimetallic complex is observed at pH~8.0 (~15%) Table shows 4.9 (vi) the calculated value of metal ligand formation constant

CONCLUSIVE REMARKS

DTPA serves as an octadentate ligand as it has eight atoms (five oxygen and three nitrogen atoms) through which, it can bind with the metal ions. The octadentate nature of DTPA in its complex was confirmed by the infrared spectral studies by Busch and Bailor⁽¹⁹³⁾. The ionization equilibria are characterized by the following values for the equilibrium constants expressed as their pK values i.e. $pK_1=27.68$, $pK_2=25.86$, $pK_3=23.21$, $pK_4=18.9$ and $pK_5=10.45$. Summation of all the pK values indicates the overall stability constant ($\log \beta$) of the homobimetallic complexes with DTPA have been presented in Table 4.11. The stability constants of Mg (II) –DTPA- M (II) systems fall in the following orders

Be (II)-DTPA < Ba (II)-DTPA < Mg (II)-DTPA < Sr (II)-DTPA < DTPA < Pb (II)-DTPA < Zn (II)-DTPA

$H_3Zn(II)$ –DTPA complex is expected to involve four coordinate tetrahedral arrangements of coordinate bonds the around Zn (II) metal ion⁽¹⁹⁴⁾. In the complex Zn (II) –DTPA, the Zn (II) is expected to bound two amino–nitrogen. It has still three vacant coordination sites available for interaction with another metal ion and thus making the formation of homobinuclear complex with DTPA

It is clear from the distribution curves that when Zn (II) and Pb (II) are complexed with DTPA in 2:1 metal to ligand ratio, the homobimetallic complex starts forming at low pH region i.e. from pH ~ 3.0 and with the increase in pH there is an increase in its concentration attaining a maximum value at pH ~ 6.0. However, when alkaline earth metal complexes are complexed with DTPA forming homobimetallic complexes the complexation starts beyond pH~6.5. Thus it may be concluded that the homobimetallic complexes with transition metals are

formed at low pH region while with alkaline earth metal ions are formed at high pH region. The complexes with transition metals exist up to 60% while with alkaline earth metals are reaching only up to 40%.

It is clearly inferred from the species distribution curves Fig 4.7 to 4.12 that no hydroxo species are found to exist except in Be (II) – DTPA system where $\text{Be}(\text{OH})^+$ and $\text{Be}(\text{OH})_2$ hydroxo species exist in small amounts.

Table 4.1

Zn(II) – DTPA (2:1) System

A. 5 ml NaNO₃ (1 M) + 5 ml HNO₃ (0.02 M) + 40 ml H₂O

B. 5 ml NaNO₃ (1 M) + 5 ml HNO₃ (0.02 M) + 5 ml DTPA (0.01 M) + 35 ml H₂O

C. 5 ml NaNO₃ (1 M) + 5 ml HNO₃ (0.02 M) + 5 ml DTPA (0.01 M) + 10 ml Zn (II) (0.01 M) + 25 ml H₂O

Overall strength of acid = 0.002 M HNO₃

Overall strength of Ligand = 0.001 M DTPA

Overall strength of Zn (II) = 0.002 M

Ionic Strength = 0.1 M NaNO₃

Strength of Alkali = 0.116 M NaOH

A		B		C	
Volume of NaOH ml.	pH	Volume of NaOH ml.	pH	Volume of NaOH ml.	pH
0.00	2.64	0.00	2.79	0.00	2.83
0.20	2.75	0.20	2.90	0.20	2.43
0.40	2.88	0.40	3.03	0.40	2.47
0.60	3.05	0.60	3.22	0.60	2.52
0.80	4.15	0.80	3.46	0.80	2.56
1.00	9.80	1.00	3.80	1.00	2.61
1.20	10.23	1.20	4.35	1.20	2.67
1.40	10.43	1.40	5.39	1.40	2.73
1.60	10.56	1.60	8.01	1.60	2.83
1.80	10.67	1.80	8.66	1.80	2.93
2.00	10.75	2.00	9.22	2.00	3.07
2.20	10.81	2.20	9.67	2.20	3.24
2.40	10.87	2.40	10.00	2.40	3.48
2.60	10.92	2.60	10.24	2.60	3.85
2.80	10.97	2.80	10.43	2.80	4.56
3.00	11.01	3.00	10.57	3.00	7.30
3.20		3.20	10.67	3.20	7.51
3.40		3.40	10.76	3.40	7.64
3.60		3.60	10.83	3.60	7.70
3.80		3.80	10.89	3.80	7.81
4.00		4.00	10.95	4.00	
4.20		4.20	11.00	4.20	
4.40		4.40	11.04	4.40	

Table 4.2

Pb(II) – DTPA (2:1) System

- A.** 5 ml NaNO_3 (1 M) + 5 ml HNO_3 (0.02 M) + 40 ml H_2O
- B.** 5 ml NaNO_3 (1 M) + 5 ml HNO_3 (0.02 M) + 5 ml DTPA (0.01 M) +
35 ml H_2O
- C.** 5 ml NaNO_3 (1 M) + 5 ml HNO_3 (0.02 M) + 5 ml DTPA (0.01 M) +
10 ml Pb (II) (0.01 M) + 25 ml H_2O

Overall strength of acid = 0.002 M HNO_3

Overall strength of Ligand = 0.001 M DTPA

Overall strength of Pb (II) = 0.002 M

Ionic Strength = 0.1 M NaNO_3

Strength of Alkali = 0.116 M NaOH

A		B		C	
Volume of NaOH ml.	pH	Volume of NaOH ml.	pH	Volume of NaOH ml.	pH
0.00	2.64	0 00	2.79	0.00	2.53
0 20	2.75	0.20	2.90	0.20	2.57
0 40	2.88	0 40	3 03	0 40	2.61
0 60	3.05	0 60	3 22	0.60	2 66
0.80	4 15	0 80	3.46	0 80	2.70
1 00	9 80	1 00	3.80	1.00	2 76
1 20	10.23	1.20	4.35	1.20	2.83
1.40	10.43	1.40	5.39	1.40	2.91
1 60	10.56	1.60	8.01	1 60	3.01
1 80	10.67	1.80	8.66	1 80	3.10
2 00	10.75	2.00	9 22	2 00	3.22
2.20	10.81	2.20	9.67	2.20	3.34
2 40	10.87	2.40	10.00	2.40	3 51
2 60	10.92	2 60	10.24	2.60	3.70
2.80	10 97	2.80	10.43	2.80	4 01
3.00	11.01	3 00	10.57	3.00	4.54
3 20		3.20	10.67	3.20	5.76
3.40		3.40	1076	3.40	7.39
3.60		3.60	10.83	3.60	7.80
3.80		3.80	10.89	3.80	8.33
4.00		4 00	10 95	4.00	9.10
4.20		4 20	11.00	4.20	9.85
4 40		4.40	11.04	4.40	10.24

Table 4.3

Be (II) – DTPA (2.1) System

- A.** 5 ml NaNO_3 (1 M) + 5 ml HNO_3 (0.02 M) + 40 ml H_2O
- B.** 5 ml NaNO_3 (1 M) + 5 ml HNO_3 (0.02 M) + 5 ml DTPA (0.01 M) +
35 ml H_2O
- C.** 5 ml NaNO_3 (1 M) + 5 ml HNO_3 (0.02 M) + 5 ml DTPA (0.01 M) +
10 ml Be (II) (0.01 M) + 25 ml H_2O

Overall strength of acid	= 0.002 M HNO_3
Overall strength of Ligand	= 0.001 M DTPA
Overall strength of Be (II)	= 0.002 M
Ionic Strength	= 0.1 M NaNO_3
Strength of Alkali	= 0.116 M NaOH

A		B		C	
Volume of NaOH ml.	pH	Volume of NaOH ml.	pH	Volume of NaOH ml.	pH
0 00	2.64	0.00	2.79	0.00	2.77
0 20	2.75	0.20	2.90	0.20	2.87
0 40	2 88	0.40	3 03	0.40	2.97
0.60	3 05	0.60	3.22	0 60	3.10
0.80	4 15	0 80	3.46	0 80	3.20
1 00	9.80	1.00	3 80	1.00	3.48
1 20	10 23	1 20	4.35	1 20	3 72
1 40	10.43	1 40	5.39	1.40	3 95
1.60	10.56	1 60	8.01	1 60	4 14
1 80	10 67	1 80	8 66	1 80	4 30
2.00	10 75	2 00	9.22	2.00	4 45
2.20	10 81	2.20	9.67	2.20	4.62
2.40	10.87	2.40	10.00	2 40	4.82
2 60	10.92	2.60	10 24	2 60	5.09
2 80	10.97	2.80	10.43	2.80	5 44
3 00	11.01	3 00	10.57	3.00	5.86
3 20		3.20	10.67	3.20	6.03
3.40		3.40	1076	3.40	6.13
3 60		3 60	10.83	3.60	6.29
3.80		3.80	10.89	3 80	6.70
4 00		4.00	10.95	4.00	7.51
4.20		4.20	11.00	4.20	8.22
4 40		4.40	11.04	4.40	8.74

Table 4.4

Mg (II) – DTPA (2:1) System

- A.** 5 ml NaNO_3 (1 M) + 5 ml HNO_3 (0.02 M) + 40 ml H_2O
- B.** 5 ml NaNO_3 (1 M) + 5 ml HNO_3 (0.02 M) + 5 ml DTPA (0.01M)
+ 35 ml H_2O
- C.** 5 ml NaNO_3 (1 M) + 5 ml HNO_3 (0.02 M) + 5 ml DTPA (0.01M)
+ 10 ml Mg(II) (0.01 M) + 25 ml H_2O

Overall strength of acid = 0.002 M HNO_3

Overall strength of Ligand = 0.001 M DTPA

Overall strength of Mg (II) = 0.002 M

Ionic Strength = 0.1 M NaNO_3

Strength of Alkali = 0.116 M NaOH

A		B		C	
Volume of NaOH ml.	pH	Volume of NaOH ml	pH	Volume of NaOH ml	pH
0 00	2 64	0 00	2 79	0.00	2 85
0.20	2 75	0.20	2.90	0.20	2 95
0.40	2.88	0.40	3.03	0.40	3 07
0.60	3.05	0.60	3.22	0.60	3.21
0 80	4.15	0.80	3.46	0 80	3 42
1.00	9 80	1.00	3.80	1.00	3.70
1 20	10.23	1.20	4.35	1.20	4.00
1 40	10 43	1.40	5.39	1.40	4.35
1.60	10 56	1.60	8.01	1.60	4.63
1 80	10.67	1.80	8.66	1.80	4.93
2 00	10 75	2 00	9.22	2 00	5 35
2.20	10.81	2 20	9 67	2.20	5 83
2.40	10.87	2.40	10.00	2.40	6.32
2.60	10.92	2.60	10.24	2.60	6 76
2.80	10.97	2 80	10.43	2.80	7.21
3.00	11.01	3.00	10 57	3.00	8.05
3.20		3 20	10 67	3.20	9.85
3.40		3 40	1076	3.40	10.24
3.60		3 60	10.83	3.60	10.44
3 80		3.80	10.89	3.80	10.58
4.00		4.00	10.95	4.00	10.68
4.20		4.20	11.00	4.20	10.72
4 40		4.40	11.04	4.40	10.78

Table 4.5

Sr (II) – DTPA (2:1) System

- A.** 5 ml NaNO_3 (1 M) + 5 ml HNO_3 (0.02 M) + 40 ml H_2O
- B.** 5 ml NaNO_3 (1 M) + 5 ml HNO_3 (0.02 M) + 5 ml DTPA (0.01 M) + 35 ml H_2O
- C.** 5 ml NaNO_3 (1 M) + 5 ml HNO_3 (0.02 M) + 5 ml DTPA (0.01 M) + 10 ml Sr(II) (0.01 M) + 25 ml H_2O

Overall strength of acid = 0.002 M HNO_3

Overall strength of Ligand = 0.001 M DTPA

Overall strength of Sr (II) = 0.002 M

Ionic Strength = 0.1 M NaNO_3

Strength of Alkali = 0.116 M NaOH

A		B		C	
Volume of NaOH ml.	pH	Volume of NaOH ml	pH	Volume of NaOH ml.	pH
0 00	2 64	0.00	2.79	0.00	2 80
0.20	2 75	0.20	2.90	0.20	2.87
0 40	2 88	0.40	3.03	0.40	2 95
0 60	3.05	0.60	3.22	0.60	3.05
0 80	4 15	0.80	3.46	0.80	3.22
1.00	9.80	1 00	3.80	1.00	3.38
1 20	10.23	1.20	4 35	1.20	3.65
1.40	10.43	1.40	5.39	1.40	4.00
1 60	10.56	1.60	8.01	1.60	4.43
1 80	10.67	1.80	8.66	1.80	5.18
2.00	10 75	2 00	9.22	2.00	5.58
2.20	10 81	2.20	9.67	2.20	5.86
2 40	10.87	2.40	10.00	2.40	6.05
2 60	10 92	2.60	10.24	2.60	6.19
2.80	10.97	2.80	10.43	2 80	6.41
3.00	11.01	3.00	10.57	3.00	6.75
3.20		3.20	10.67	3 20	7 91
3 40		3.40	1076	3.40	7 90
3 60		3.60	10.83	3.60	10.26
3 80		3 80	10.89	3.80	10.47
4 00		4 00	10 95	4.00	10.61
4 20		4.20	11.00	4.20	10.69
4.40		4.40	11.04	4.40	10.78

Table 4.6

Ba (II) – DTPA (2:1) System

- A.** 5 ml NaNO_3 (1 M) + 5 ml HNO_3 (0.02 M) + 40 ml H_2O
- B.** 5 ml NaNO_3 (1 M) + 5 ml HNO_3 (0.02 M) + 5 ml DTPA (0.01 M) + 35 ml H_2O
- C.** 5 ml NaNO_3 (1 M) + 5 ml HNO_3 (0.02 M) + 5 ml DTPA (0.01 M) + 10 ml Ba (II) (0.01 M) + 25 ml H_2O

Overall strength of acid = 0.002 M HNO_3

Overall strength of Ligand = 0.001 M DTPA

Overall strength of Ba(II) = 0.002 M

Ionic Strength = 0.1 M NaNO_3

Strength of Alkali = 0.116 M NaOH

A		B		C	
Volume of NaOH ml	pH	Volume of NaOH ml.	pH	Volume of NaOH ml.	pH
0.00	2.64	0.00	2.79	0 00	2 72
0.20	2 75	0 20	2 90	0.20	2 83
0.40	2.88	0.40	3.03	0.40	2 93
0.60	3 05	0.60	3 22	0.60	3.08
0 80	4.15	0.80	3 46	0 80	3.29
1 00	9 80	1 00	3.80	1.00	3 57
1.20	10.23	1.20	4.35	1.20	3.99
1.40	10.43	1.40	5.39	1.40	4.61
1 60	10.56	1.60	8.01	1.60	5.73
1.80	10.67	1.80	8.66	1.80	3.13
2 00	10 75	2 00	9 22	2.00	36.38
2 20	10 81	2.20	9.67	2.20	6.61
2 40	10 87	2.40	10.00	2.40	6.88
2.60	10.92	2.60	10.24	2.60	7.57
2 80	10.97	2.80	10.43	2.80	9.70
3.00	11.01	3 00	10.57	3.00	10.18
3 20		3 20	10.67	3.20	10.45
3.40		3.40	1076	3.40	10.61
3 60		3.60	10.83	3.60	10.73
3.80		3.80	10 89	3 80	10.81
4.00		4 00	10 95	4.00	10.88
4.20		4.20	11.00	4.20	10.95
4 40		4.40	11.04	4.40	11.01

Table 4.7

Proton –Ligand formation constant ($\log \beta_{\text{overall}}$) of DTPA at $\pm 37 \text{ }^{\circ}\text{C}$ and $\mu=0.1 \text{ mole dm}^{-3} \text{ NaNO}_3$.

S.NO.	Species	p	q	r	s	t	$\log \beta$
(i)	H ₅ L	0	0	1	0	-5	27.68
(ii)	H ₄ L	0	0	1	0	-4	25.86
(iii)	H ₃ L	0	0	1	0	-3	23.21
(iv)	H ₂ L	0	0	1	0	-2	18.98
(v)	HL	0	0	1	0	-1	10.45

Table 4.8

Hydrolytic constants of Be²⁺ aq. ion

S NO	Species	p	q	r	s	t	$\log \beta$
(i)	Be (OH) ⁺	1	0	0	0	1	-5.70
(ii)	Be (OH) ₂	1	0	0	0	2	-11.16

Table 4.9

Zn (II)-DTPA-Zn (II)

Metal –Ligand formation constant: Homobimetallic (2:1) system

S NO	Species	p	q	r	s	t	log β
(i)	Zn (II)-DTPA	2	0	1	0	0	22.76
(ii)	Pb(II)-DTPA	2	0	1	0	0	22.06
(iii)	Be (II)-DTPA	2	0	1	0	0	9.64
(iv)	Mg (II)-DTPA	2	0	1	0	0	10.36
(v)	Sr (II)-DTPA	2	0	1	0	0	10.68
(vi)	Ba (II)-DTPA	2	0	1	0	0	9.75

Table 4.10

Stability constant values for the metal-ligand (2:1) complexes: homobimetallic system	
Reaction (metal- ligand (2:1))	log β
$\text{Zn}^{2+} + \text{DTPA}^{5-} \rightleftharpoons [\text{Zn-DTPA-Zn}]^{-}$	22.79
$\text{Pb}^{2+} + \text{DTPA}^{5-} \rightleftharpoons [\text{Pb-DTPA-Pb}]^{-}$	22.06
$\text{Be}^{2+} + \text{DTPA}^{5-} \rightleftharpoons [\text{Be-DTPA-Be}]^{-}$	9.64
$\text{Mg}^{2+} + \text{DTPA}^{5-} \rightleftharpoons [\text{Mg-DTPA-Mg}]^{-}$	10.36
$\text{Sr}^{2+} + \text{DTPA}^{5-} \rightleftharpoons [\text{Sr-DTPA-Sr}]^{-}$	10.68
$\text{Ba}^{2+} + \text{DTPA}^{5-} \rightleftharpoons [\text{Ba-DTPA-Ba}]^{-}$	9.75

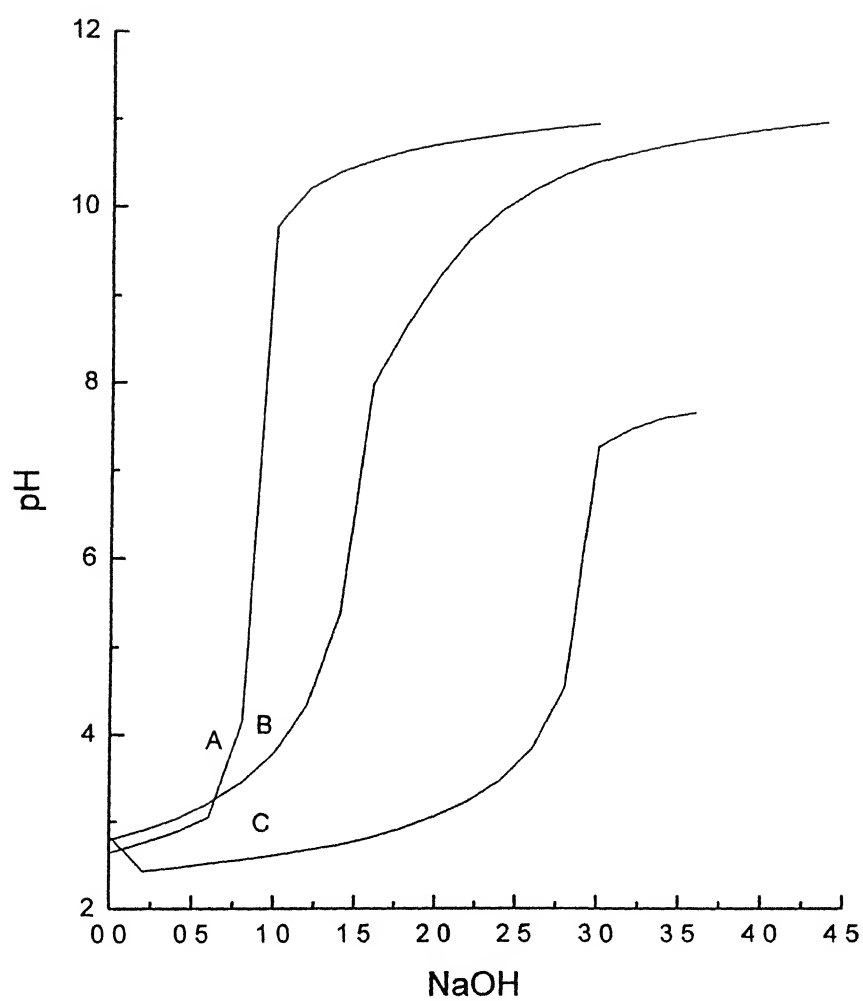


Fig. 4.1 Titration curves of Zn(II)-DTPA (2:1) System.

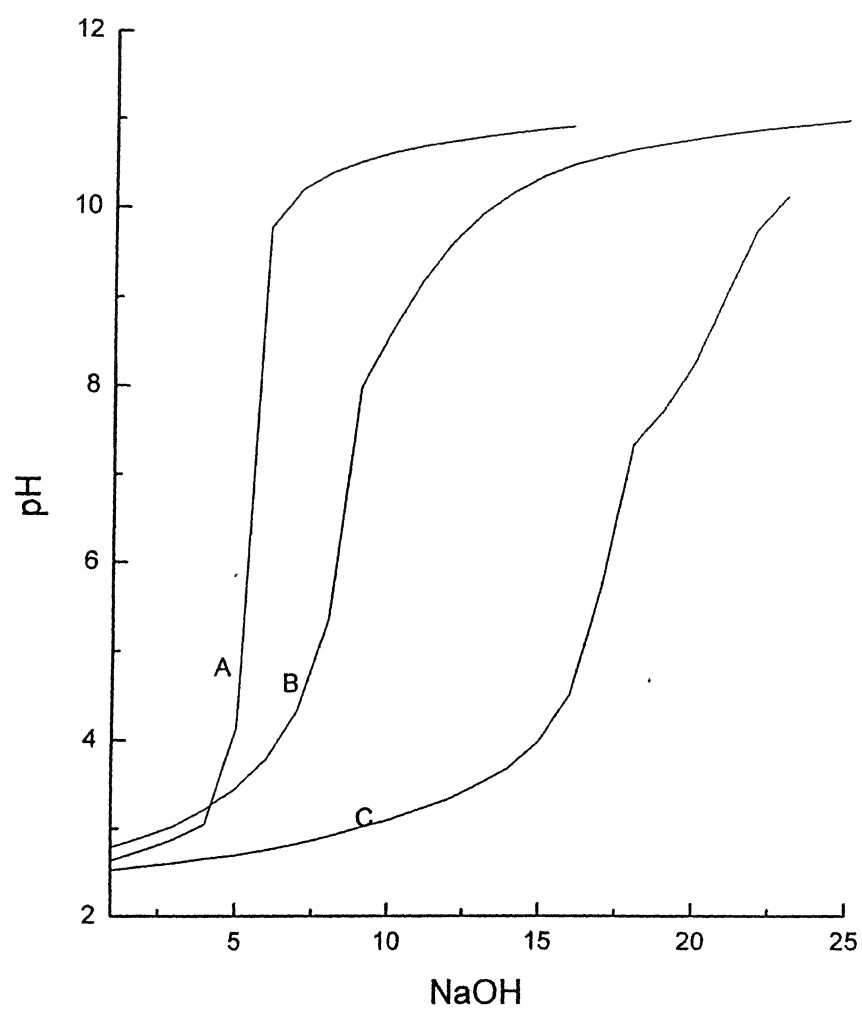


Fig.4.2 Titration curves of Pb(II)-DTPA (2:1) System.

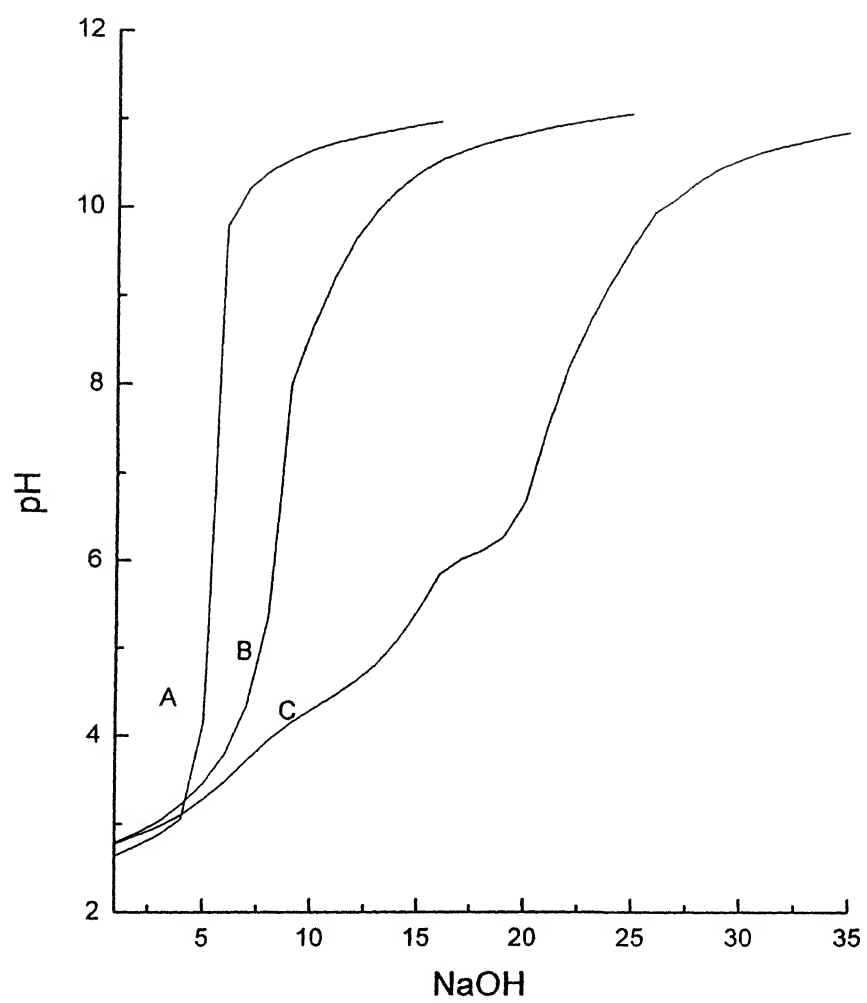


Fig. 4.3 Titration curves of Be(II)-DTPA (2:1) System.

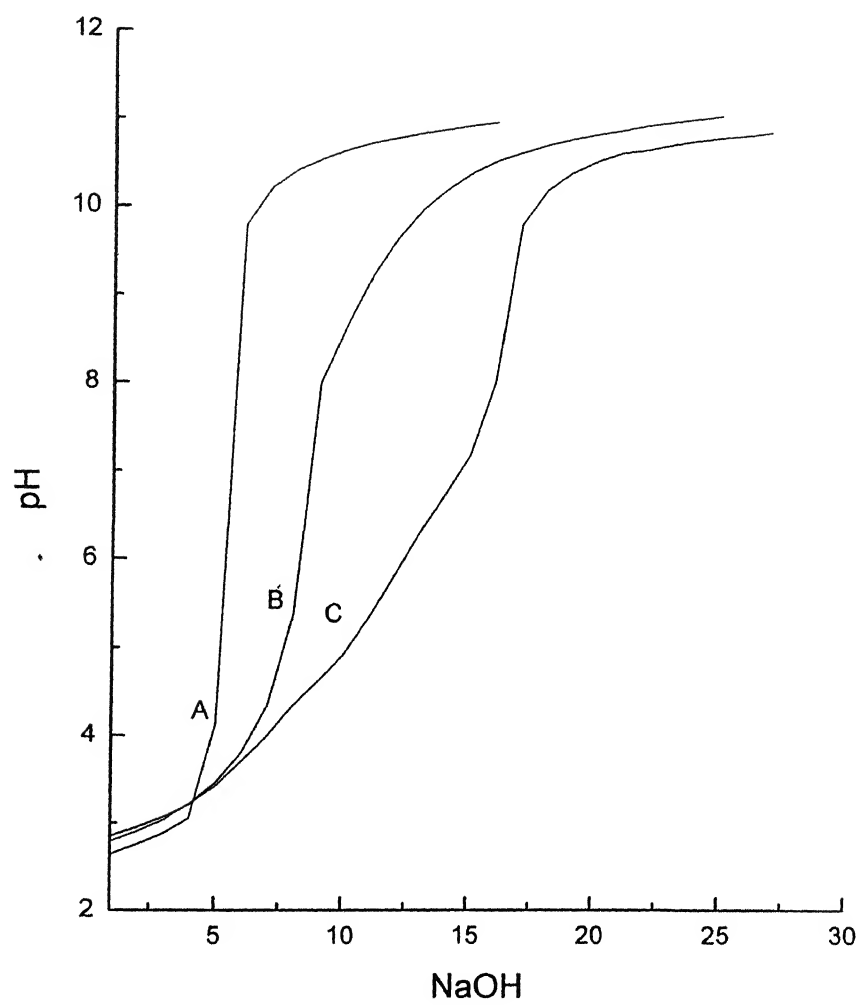


Fig. 4.4 Titration curves of Mg(II)-DTPA (2:1) System.

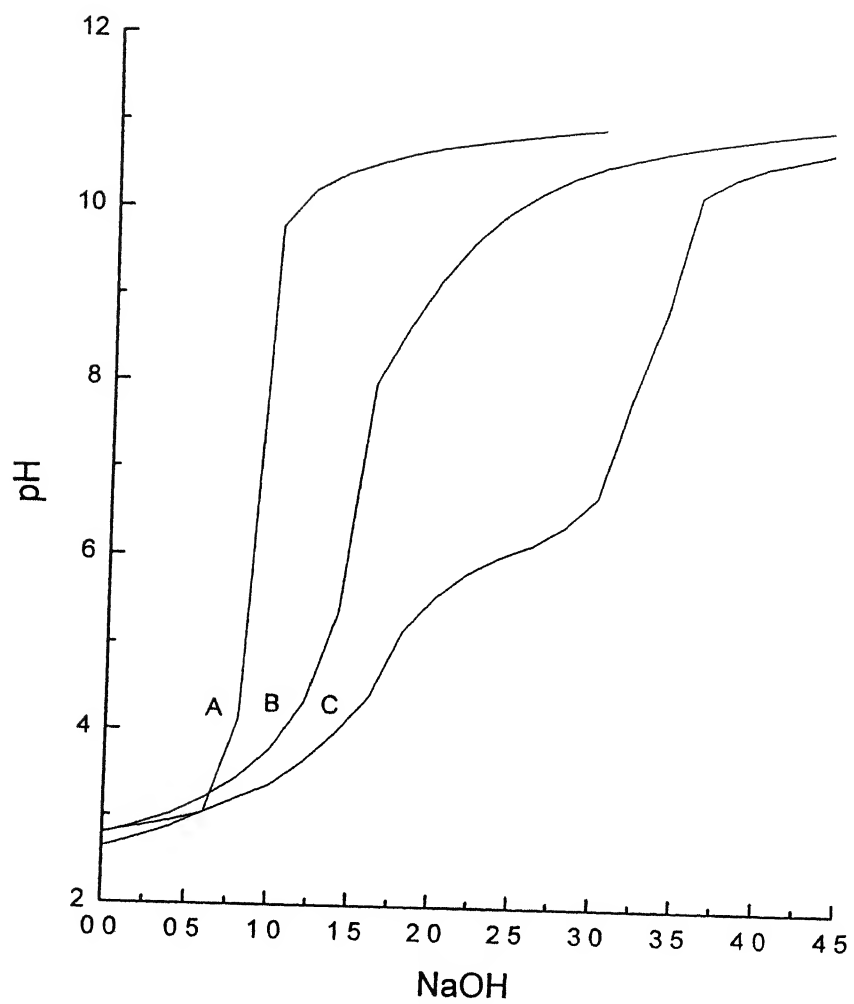


Fig. 4.5 Titration curves of Sr(II)-DTPA (2:1) System.

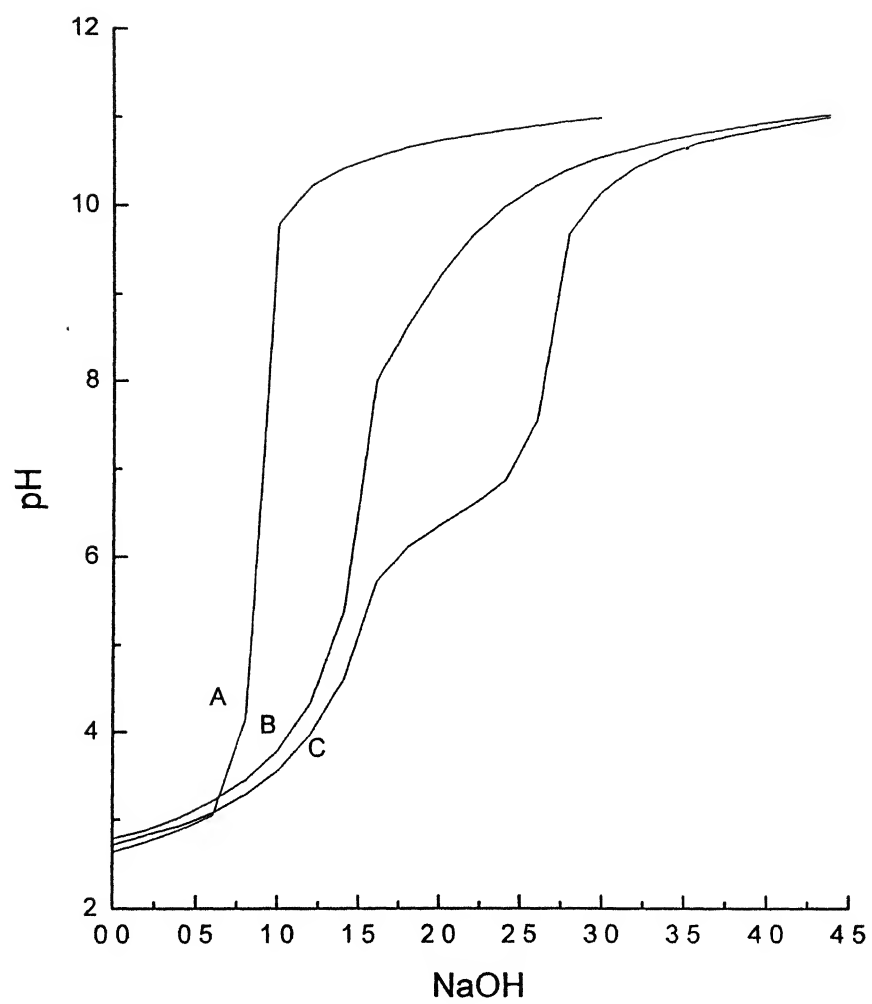


Fig.4.6 Titration curves of Ba(II)-DTPA (2:1) System.

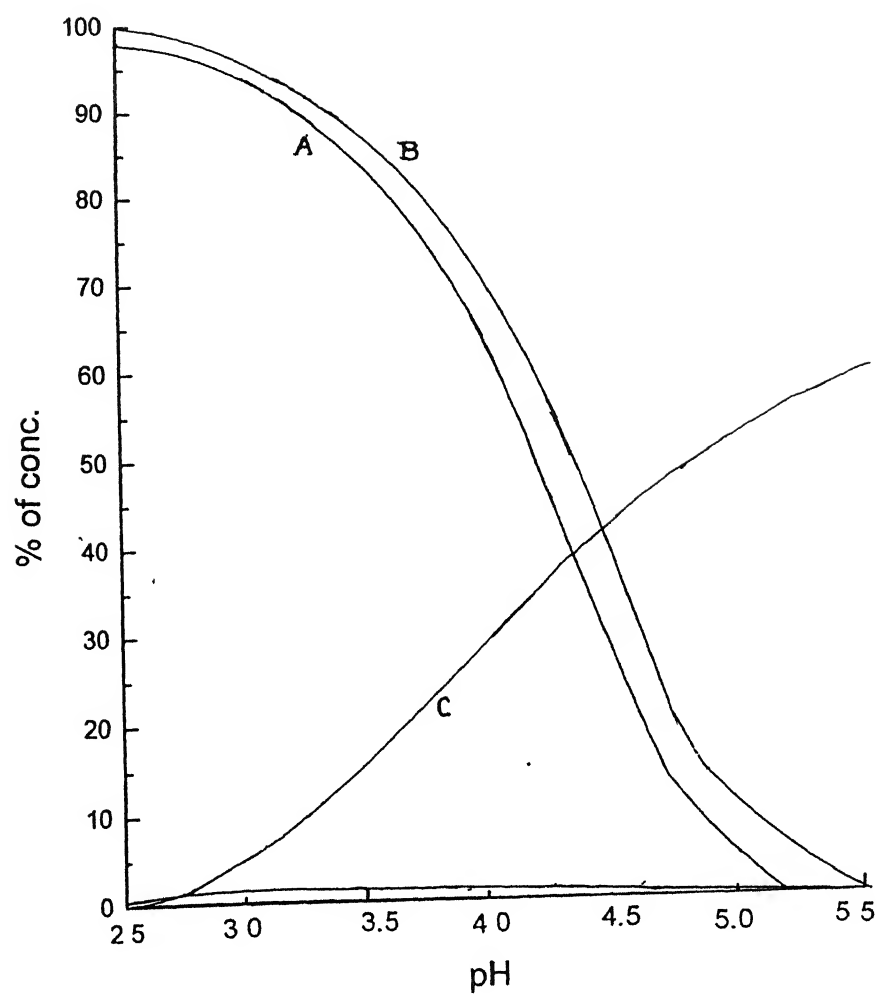


Fig. 4.1. Species distribution curve of Zn(II)-DTPA (2:1) System
Where (A) H₃L (B) Zn(II) (C) Zn(II)-DTPA .

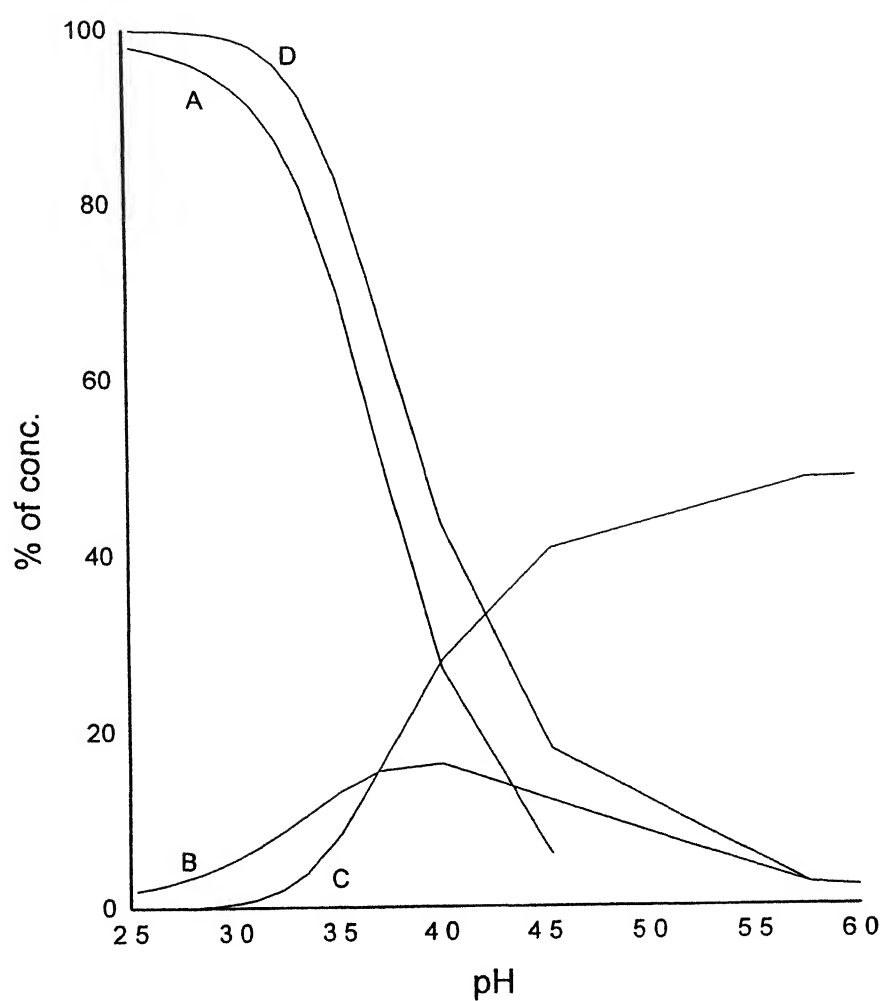


Fig. 4.8 Species distribution curve of Pb(II)-DTPA(2:1) System
Where (A) H₃L (B) H₂L (C) Pb(II)-DTPA (D) Pb(II).

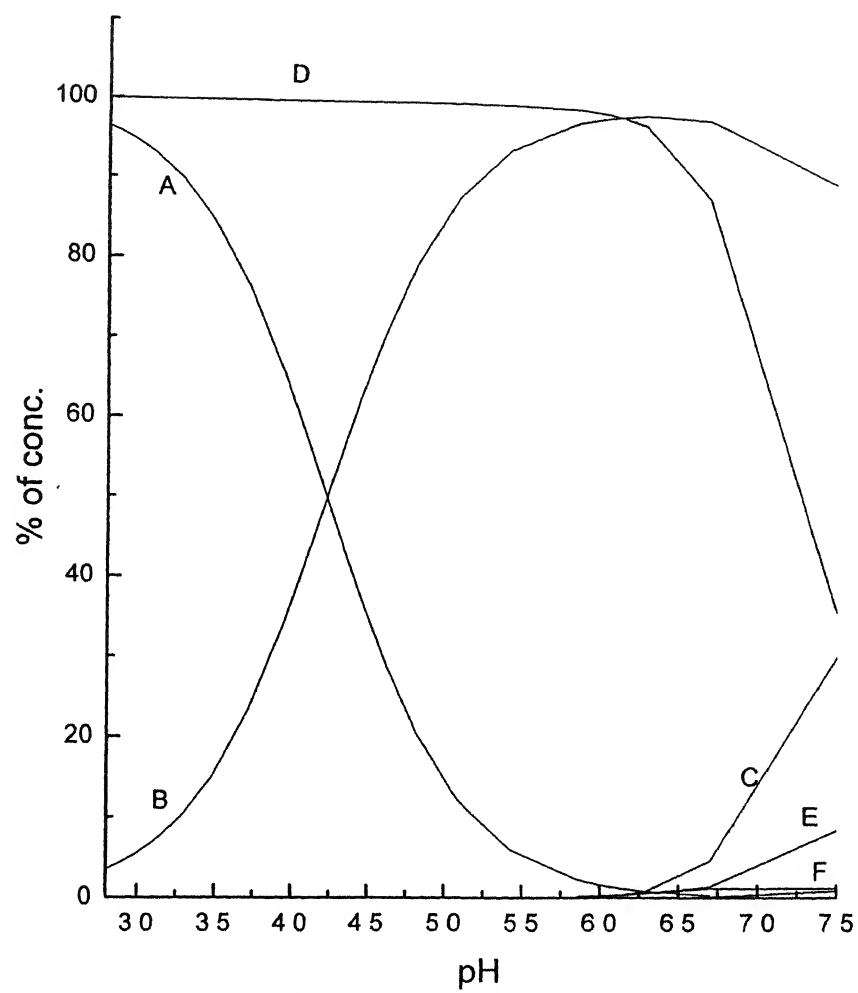


Fig 4 9. Species distribution curve of Be(II)-DTPA (2 1) System
Where (A) H_3L (B) H_2L (C) Be(II)-DTPA (D) Be(II) (E) Be(OH)+ (F) Be(OH)₂

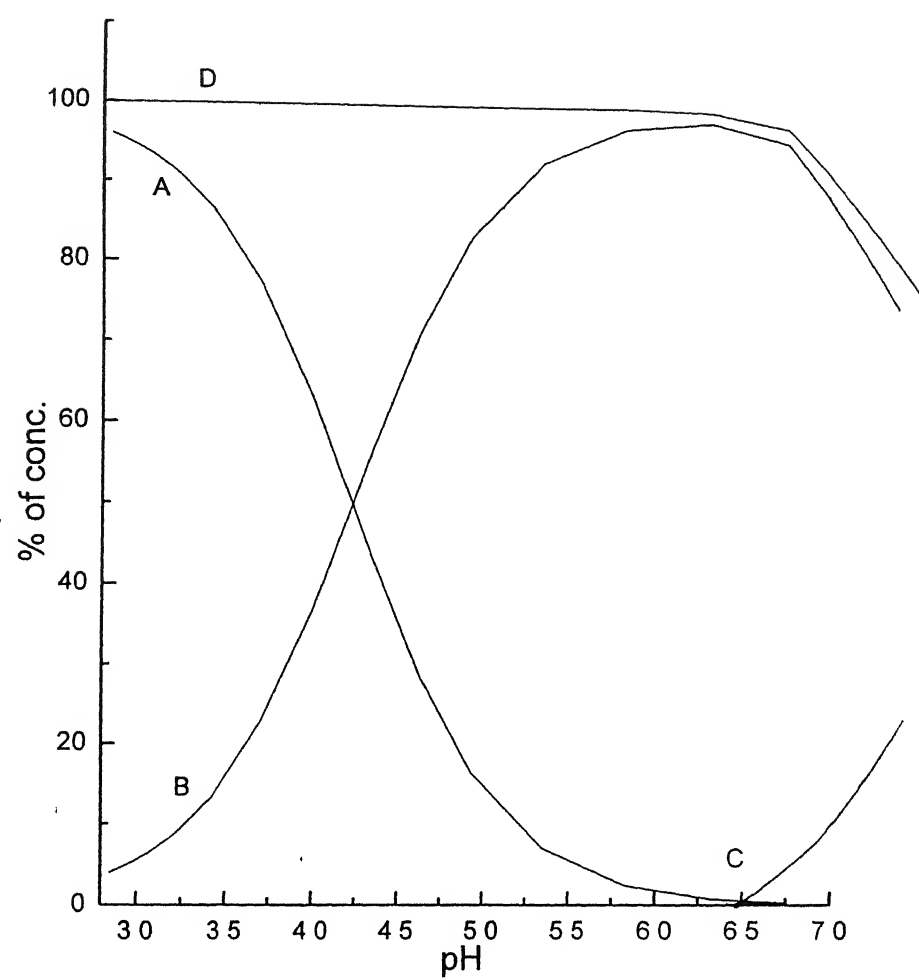


Fig 4 10 Species distribution curve of $Mg(II)$ -DTPA (2:1) System
Where (A) H_3L (B) H_2L^- (C) $Mg(II)$ -DTPA (D) $Mg(II)$

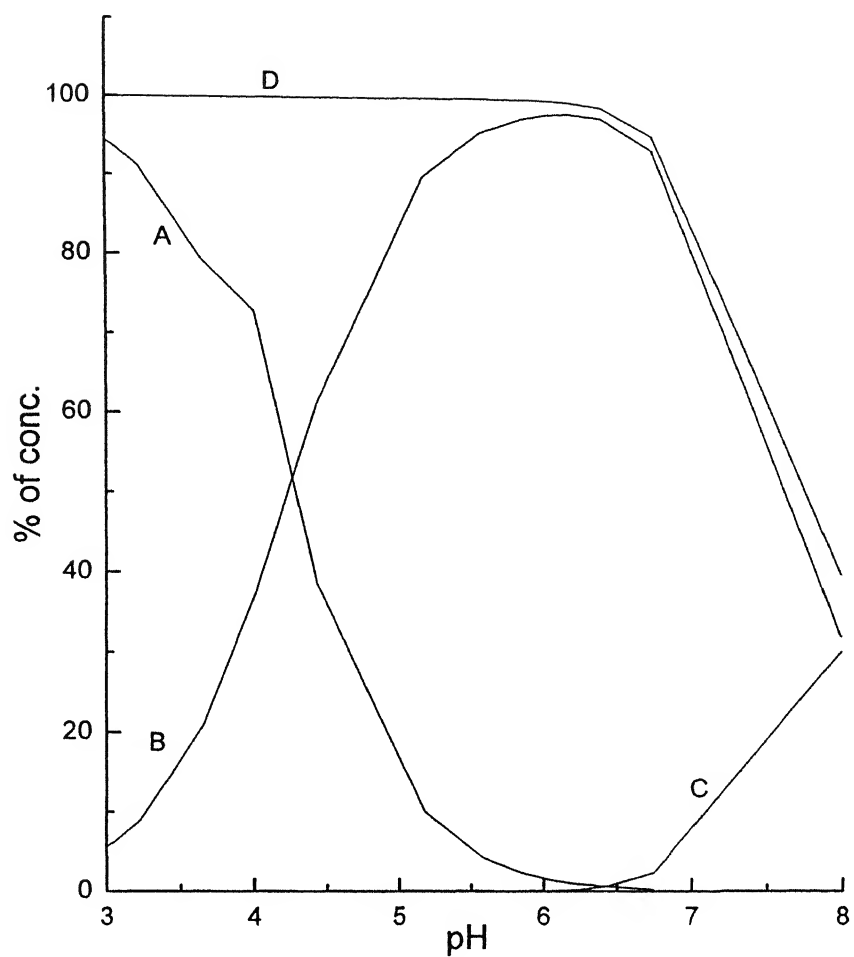


Fig 4 11 Species distribution curve of Sr(II)-DTPA (2:1) System
Where (A) H_3L (B) H_2L (C) Sr(II)-DTPA (D) Sr(II)

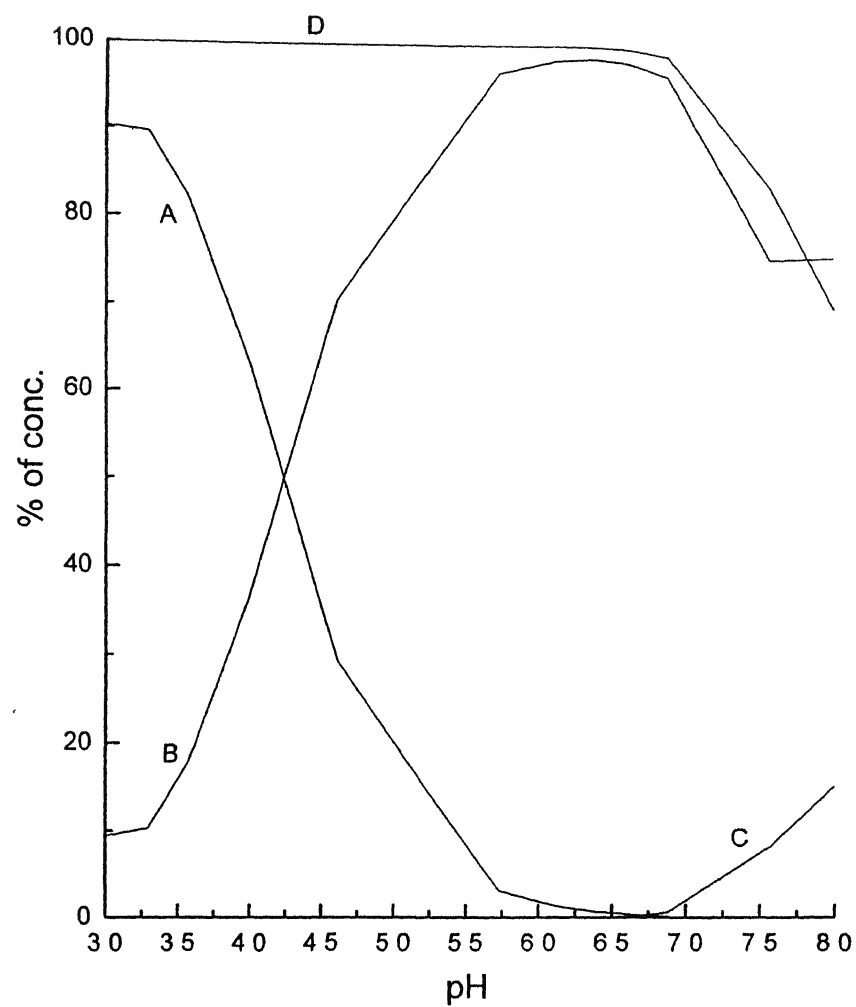


Fig 4 {2 Species of distribution curve of Ba(II)-DTPA (2 1) System
Where (A) H₃L (B) H₂L (C) Ba(II)-DTPA (D) Ba(II)

CHAPTER V

FORMATION EQUILIBRIA OF HETEROBIMETALLIC SYSTEMS

The present chapter deals with the heterobinuclear complexes⁽¹⁹⁵⁾ formed by Diethylenetriaminepenta acetic acid (DTPA) with Zn (II) -L -CO (II), Zn (II) -L -Ni (II), Zn (II) -L -Cu (II), Zn (II) -L -Cd (II), Zn (II) -L -Be (II), Zn (II) -L -Mg (II), Pb (II) -L -Be (II) and Pb (II) -L -Mg (II) systems in aqueous medium at $37 \pm 1^\circ$ and $\mu = 0.1 \text{ mol dm}^{-3} \text{ NaNO}_3$. The relevant stability constants have been evaluated using SCOGS Computer program.

Titration Procedure:

Four reaction mixtures were prepared by keeping the total volume 50 ml in each case and the molar ratio of ligand, primary and secondary metals undertaken was kept 1 : 1 : 1.

Sol A. 5 ml HNO_3 (0.2 M) + 5 ml NaNO_3 (1M) + 40 ml water

Sol B 5 ml HNO_3 (0.2 M) + 5 ml NaNO_3 (1M) + 5 ml DTPA (0.1) + 35 ml water

Sol C 5 ml HNO_3 (0.2 M) + 5 ml NaNO_3 (1M) + 5 ml DTPA (0.01M) + 5 ml $M_1(\text{II})$ (0.01M) + 30 ml water

Sol D 5 ml HNO_3 (0.2 M) + 5 ml NaNO_3 (1M) + 5 ml DTPA (0.01M) + 5 ml $M_1(\text{II})$ (0.01M) + 5 ml $M_2(\text{II})$ (0.01M) + 25 ml water

The pH titration data are presented in Table 5.1 to 5.8 and the titration curves are shown in Figures 5.1 to 5.8. The plot of pH against the volume of alkali gives the titration curves A, B, C & D corresponding to acid, DTPA, the $M(\text{II})$ -DTPA and the $M_1(\text{II})$ -DTPA- $M_2(\text{II})$ mixed metal ions complex respectively (where $M_1 = \text{Zn}(\text{II})$, Pb (II) as primary metal and $M_2 = \text{CO}(\text{II})$, Ni (II), Cu (II), Cd (II), Be (II) and Mg (II) as secondary metal ions. It is clear from the titration

curves that initially binary complex Zn (II)- DTPA and Pb(II) - DTPA are formed. Formation of such binary complex in solution is deduced from the displacement of metal titration curves with respect to the ligand titration curves along the volume axis. Thus, deprotonation of the ligand is explained by the coordination of metal ion with the ligand.

The formation of ternary complex is deduced from the fact that the curve corresponding to mixed metal species diverges from the titration curves corresponding to primary metal i.e. Zn (II) and Pb (II) right from the beginning of the titration. This is due to chelation, where another protons of the ligand are displaced by the second metal ions.

From the titration curves A (acid) and B (ligand) \bar{n}_H values at various pH were calculated and the curve between the pH and corresponding \bar{n}_H values was obtained. The curve extends from $\bar{n}_H = 0$ to $\bar{n}_H = 2.5$. This indicates⁽¹⁹⁶⁾ three step dissociation of the ligand. The \bar{n}_H values at various pH are given in the table.

\bar{n}_H table for ligand DTPA

pH	\bar{n}_H	pH	\bar{n}_H
2.0	2.85	4.4	0.74
2.2	2.61	4.6	0.67
2.4	2.40	4.8	0.64
2.6	2.10	5.0	0.58
2.8	1.85	5.2	0.54
3.0	1.67	5.4	0.51
3.2	1.52	5.6	0.48
3.4	1.37	5.8	0.45
3.6	1.20	6.0	0.44
3.8	1.02	6.2	0.42
4.0	0.94	6.4	0.42
4.2	0.84	6.6	0.42

Species Distribution Curves: -

Species distribution curves are obtained by plotting % concentration of the species obtained through SCOGS computer technique against pH. The distribution curves are finally sketched by running the computer program ORIGIN 4.0 and are shown in Fig 5.9 to 5.16.

The distribution of binary system has also been sketched and studied in order to explain the comparative chelating behavior of the ligand towards both the metal ions taken under study.

Proton- ligand formation constants :

The proton - ligand formation constants of DTPA have been determined by Irving- Rossotti titration technique and are presented in Table 5.9, DTPA shows five replaceable protons. The proton-ligand formation constants reported here agree with the literature values ⁽¹⁹⁷⁾.

Metal -ligand formation constants:

The metal - ligand formation constants of binary and ternary complexes were evaluated using computer program. The refined values of $\log \beta$ of binary, hydrolytic species and estimated values of $\log \beta_{11100}$ for the ternary complexes were supplied to the computer as the input data. The Tables 5.10 to 5.18 represent the refined values of binary, hydroxo and ternary complex species of binary and ternary Zn (II)-DTPA- M (II) and Pb (II)-DTPA-M (II) systems taken under study. Preliminary values of some of the constants supplied to the computer as input data were calculated by analysing the pH - titration curves. The computer gives the values of the constants ($\log \beta_{pqrst}$) and also

the concentration distribution of the complex species at different pH values as the output described further

Zn(II)- DTPA-Co(II) (1:1:1) System

Fig 5 1 and Fig 5 9 represent the titration and species distribution curves of the present ternary system respectively. Proton ligand formation constants Table 5 9 of the ligand DTPA have been taken from the literature, metal ligand formation constants of the binary and ternary systems have been calculated and refined by calvin Bjerrum technique employing the method of by Irving and Rossotti using SCOGS computer program and are presented in Table5 11.

Species distribution curves provide the existence of following species

- (i) **Protanated species of the ligand**
- (ii) **Free metal ions**
- (iii) **Binary complexes**
- (iv) **Ternary complex.**

(i) Protanated species of the ligand

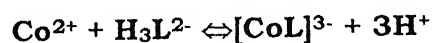
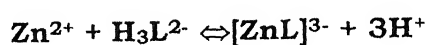
Only H_3L species of the ligand is remarkably present in the pH range 1.76- 3.4 Its concentration decreases with the increase in pH AT pH ~ 3.4 its concentration is negligible

(ii) Free metal ions

Nearly 40% Zn (II) and 35% Co (II) are present in free state at the beginning of the titration With the rise in pH, their concentration are found to decrease reaching up to 20% and 7% respectively at pH 3.5.

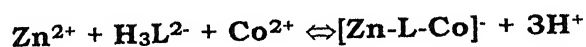
(iii) Binary Complex.

Two types of binary complex species are present i.e Zn (II) – DTPA and Co (II) –DTPA. The concentration of both the complex species are found to increase gradually with the rise in pH upto 3.4 and thereafter remaining constants. Maximum concentration of Zn (II) –DTPA and Co (II) –DTPA binary species are $\approx 5\%$ and $\approx 19\%$ respectively



(iv) Ternary complex

Ternary mixed metal complex is the major predominant species in the present system showing its existence in the entire pH range. Its formation starts from the beginning of the titration where its concentration is found to be nearly 59%. There is a gradual increase in its concentration with the increases in pH attaining a maximum concentration of $\approx 73\%$. Its formation is defined by the equilibrium



It is clear from the species distribution diagram that there is a simultaneous process of complex formation i.e binary and ternary complexation starts from the very beginning of the titration

Zn(II)- DTPA-Ni(II) (1:1:1) System

Titration curves and species distribution curves of the present ternary system are given in Fig 5.2 and Fig. 5.10 respectively. Metal ligand formation constants of the binary and ternary systems are

presented in Table 5.12. Formation of hydroxo species were also considered in calculating the equilibrium constant but as the hydrolytic equilibria of Zn (II) and Ni (II) are not found to be overlapping with the buffer regions corresponding to metal ligand formation equilibria of binary and ternary complexes, therefore, their existence are ruled out. Following species are identified in Zn (II) - DTPA-Ni (II) system

- (i) **Protonated species of the ligand.**
- (ii) **Free metal species**
- (iii) **Binary metal-ligand complex.**
- (iv) **Mixed- metal complex.**

(i) Protonated species of the ligand:

H₃L species of the ligand is identifiable in the present system in the pH range 2.25-3.2. Its concentration gradually decreases with the increase in pH. Buffer region at pH > 2.25 may be metal induced deprotonation of the ligand. (proton-ligand formation constants present in Table 5.9)

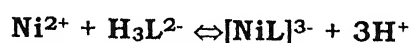
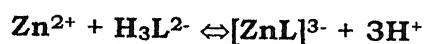
(ii) Free metal species:

Zn (II) and Ni (II) in the free state are found to exist in the decreasing order with the increase in pH. This indicates their involvement in the process of complexation. Free metal species are identifiable in the pH range 2.25- 3.5. At pH > 3.5 their concentrations are negligible.

(iii) Binary metal- ligand species:

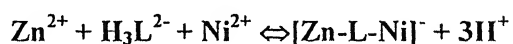
Two types of binary species are identified appreciably in the present system. There is a gradual increase in the concentration of both the complexes i.e. Zn(II)- DTPA and Ni(II) – DTPA with the

increase in pH. Maximum concentration of Zn (II) –DTPA complex is ~5% at pH ~3.5 and of Ni (II) –DTPA complex is ~49% at pH ~3.5. Their formation takes place following the equilibria



(iv) Mixed- Metal Complex

Ternary heterobinuclear complex Zn(II)- DTPA- Ni(II) shows its existence in fairly good concentration, maximum concentration of it being nearly 46% at pH~2.6. Its formation starts from pH~ 2.25, increases gradually with the increase in pH and thereafter remains constant. Ternary complexation is defined according to the equilibrium



Species distribution curves indicate that there is a simultaneous process of complex formation i.e. the binary and ternary complexes are formed right from the beginning of the titration.

Zn(II)– DTPA–Cu(II) (1:1:1) System

Fig. 5.3 and Fig 5.11. Represent the titration and speciation curves of the present ternary system respectively. Proton-ligand formation constants of DTPA have already been given in Table 5.9. Metal-ligand formation constants of binary and ternary systems are given in Table 5.13.

Fig 5.11 define the existence of following general species along with the ternary complex -

- (i) **H₃L species.**
- (ii) **Free metal species.**
- (iii) **Binary complex species.**
- (iv) **Ternary complex**

(i) H₃L species

Only H₃L species is present as the protonated species of the ligand DTPA in the pH range 2.25-3.0. This indicates the possibility of complexation only in the very low pH region.

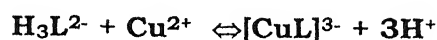
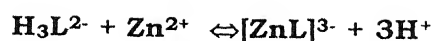
(ii) Free metal species

Both the free metal species Zn (II) and Cu (II) i.e present in decreasing order of their concentrations with the rise in pH. This shows their involvement in binary and ternary complex formation. However, only ≈18% of Zn (II) is involved in complexation while, almost 95% Cu (II) is utilized in the process of complex formation.

(iii) Binary complex species.

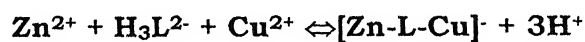
Very small concentration of Zn (II) –DTPA binary complex is existing in the present system. Its formation starts from pH~2.25 where it is almost negligible and gradually increases up to pH~ 3.0 (≈4%).

Minimum concentration of Cu (II) –DTPA complex is observed at pH~2.25 (≈85%). Which after a gradual increase attains a maximum value at pH~ 3.0 (≈90%).



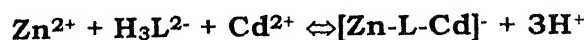
(iv) Ternary Complex.

As it is clear from the speciation curves that almost all the Zn(II) and Cu(II) species are coordination with the ligand to form binary complexes while only a very small amount of Zn(II) and Cu(II) are involved simultaneously with the ligand to form ternary 1:1:1 complex. Only $\approx 4\%$ ternary complex exists at the starting pH, which gradually increases attaining a maximum concentration ($\approx 7\%$) at pH ~ 3.0 . Therefore its concentration remains constant.



Zn (II)– DTPA–Cd (II) (1:1:1) System

Ternary 1:1:1 Zn (II) –DTPA–Cd (II) complex is the predominating species in the present system (table 5.14) which shows its formation in the pH range 2.25–3.5. There is a gradual incline in the concentration of mixed metal complex with the rise in pH. Following equilibrium defines the formation of ternary complex:



Besides, the ternary complex, following species are evident

- (i) **Protonated ligand species**
- (ii) **Free metal ions**
- (iii) **Binary complex.**

(i) Protonated ligand species (i.e. H_3L):

H_3L species of the ligand exists in the pH range 2.25-3.3. There is a gradual decrease in its concentration with the increase in pH. Buffer region at pH > 2.3 may be metal ions induced deprotonation of the ligand. The proton-ligand formation constants shown in Table 5.9.

(ii) Free metal ions

Both the metal ions Zn (II) and Cd (II) are also identified in the pH range 2.25-3.5 in the decreasing order of their concentrations.

(iii) Binary Complex

Both the metal ions are found to coordinate with the ligand forming binary complexes. Zn (II) –DTPA and Cd (II) –DTPA complexes are formed in the pH range 2.25-3.5. The concentration of both the binary complexes species increase with the rise in pH. Beyond pH ~3.5, their concentrations remain almost constant.

Binary complexation is governed according to the following equilibria



It is clear from the species distribution diagram Fig. 5.12 that both the binary and ternary complexes are formed simultaneously at the beginning of the titration.

Zn (II) -DTPA-Be (II) (1:1:1) system-

Fig 5 13 is the species distribution diagram of the present system. Titration curves are given in fig 5.5 proton -ligand formation constants of the ligand have already been given in Table 5 9. Metal- ligand formation constants of binary and ternary complexes are given in Table 5.13.

Divergence of mixed metal titration curve D from the metal- ligand titration curve C and the distribution profiles of Fig.5.5 clearly indicate the formation heterobinuclear complex Zn(II)-DTPA-Be(II) in the pH range 2.5- 3.5. Beyond pH ~3.5 its concentration becomes constant up to pH~5.0. The minimum concentration of this complex is ~88% which after a gradual increase exceeds up to ~96% at pH ~ 3.5.

Following species are also identifiable along with the mixed metal complex

- (i) **Protonated ligand species**
- (ii) **Free metal species**
- (iii) **Binary complex species**
- (iv) **Hydroxo species**

(i) Protonated Ligand Species

The proton-ligand formation constants of DTPA were determined by Calvin-Bjerrum's technique employing the technique of Irving and Rossetti. The metal-ligand formation constants of the binary and ternary complexes were evaluated using SCOGS computer program.

Only H_3L species of the ligand shows its marked presence. Its concentration decreases gradually with the increase in pH, maximum

concentration of it being $\approx 13\%$ at $\text{pH} \sim 2.5$ H_2L species is present in traces

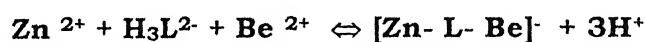
(ii) Free Metal Species

Both the metal species are present in the free state in the decreasing order of their concentration, which shows their involvement in the process of complexation

(iii) Binary Complex Species:

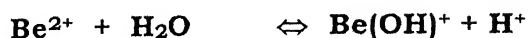
Only Zn (II)- DTPA binary complex shows its existence in the entire region. A steep fall in the concentration of Zn(II) in comparison to Be(II) with the rise in pH shows its involvement in both the binary and ternary complexation

Binary and ternary complexation equilibria may be defined as:



(iv) Hydroxo Species

Formation of hydroxo species are also considered in the present system as it is clear from the speciation curves the buffer regions corresponding hydrolytic equilibria parallel the metal-ligand equilibria of ternary complex. Two types of hydrolytic species are formed beyond pH 5.0 according to the following equilibria.



Zn (II) –DTPA–Mg (II) (1:1:1) system:

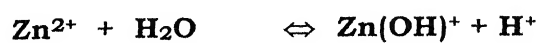
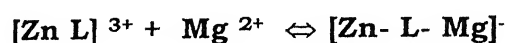
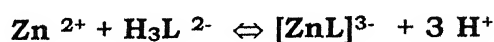
Ternary complex of DTPA (diethylenetriaminepentaacetic acid) with Zn (II) and Mg (II) has been investigated using potentiometry in aqueous medium at 25 ± 10 and $\mu = 0.1$ NaNO₃. The experimental data have provided evidence for the following general species (L=DTPA, M₁ = Zn (II), M₂ = Mg (II)), HL, H₂L, H₃L, M₁L, M₂L & M₁ M₂L along with the various hydroxo species. pH-metric titration curves are shown in Fig 5.6. Proton-ligand formation constants, and metal-ligand formation constants are given in Table 5.9 and 5.16 respectively.

Proton-Ligand formation constants

The species distribution curves are shown in Fig 5.14. Proton ligand formations constant for DTPA are given in Table 5.9. DTPA shows five replaceable protons. The proton-ligand formation constants reported here agree with the earlier reported values.

Metal-Ligand Formation Constants

The values of $\log \beta$ for the binary and ternary complex formation reactions are listed in Table 5.16.



The pH titration curve and species distribution curve fig2 of this ternary system indicates that Zn (II)-DTPA-Mg (II) type of ternary species is present

Speciation curves indicate the formation of (1 1 1) ternary complex in the pH range 2.5 to 3.5 according to the equilibrium, presented earlier

Minimum concentration of Zn (II) -L-Mg (II) is evident at pH 2.5 (58%) which gradually increases up to its maximum concentration (80%) at pH 3.5 and there after remains constants from pH 3.5 to 5.0

Besides Zn (II) -L -Mg (II) ternary complex species are found to exist in the present system

(1) Protonated Ligand Species

H₃L: - As the concentration of ternary complex and binary complex increases, the concentration of protonated ligand species H₃L is found to exist in decreasing order. The concentration of H₃L species is maximum (≈36%) at pH 2.5 and declines up to negligible concentration (1%) till pH 3.80. H₂L species exist in negligible amounts

(2) Free Metal Ions

The species distribution curves shows that the primary metal Zn²⁺ and secondary metal Mg²⁺ as free metal ions are present in decreasing order of their concentration with increase in the concentration of binary and ternary complexes. The maximum concentration of primary free metal ion (Zn (II)-DTPA) is (36%) which gradually decreases up to 0% in the entire pH range of 2.5 to 4.0.

Similarly the maximum concentration of secondary free metal ion (Mg^{2+}) is (42%) at pH 2.5, which gradually decreases up to 19% till pH 4.5

Pb (II) –DTPA–Be(II) system–(1:1:1) ratio

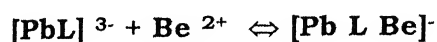
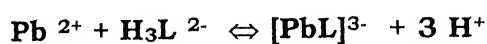
Ternary complex of DTPA (diethylene triamine pentaacetic acid) with Pb (II) and Be(II) has been investigated using potentiometry. The experimental data have provided evidence for the following general species ($\text{L}=\text{DTPA}$), $\text{M}_1 = \text{Pb(II)}$, $\text{M}_2 = \text{Be(II)}$, HL , H_2L , H_3L , M_1L , M_2L & $\text{M}_1\text{M}_2\text{L}$ along with various hydroxo species. pH-metric titration curves are shown in Fig 5.7. Proton- ligand formation constants, hydrolytic constants and metal- ligand formation constants are given in Table 5.9, 5.10 and 5.17 respectively.

1.2 (Proton–Ligand formation constants:

The species distribution curves are shown in Fig 5.15. Proton-ligand formation constant for DTPA is given in Table 5.9. DTPA shows five replaceable protons. The proton ligand formation constants reported here agree with the earlier reported values (or literature values).

1.3–metal ligand formation constants:

Values of $\log \beta$ for the binary and ternary complex formation reactions are listed in Table 5.17



The pH titration curve Fig 5.7 and species distribution curve Fig. 5.15 of this ternary system indicates that Pb(II)-DTPA-Be(II) type of ternary species is present.

Speciation curves indicate the formation of (1:1:1) ternary complex in the pH range 2.5 to 3.5 according to above minimum concentration of Pb(II) : L : Be(II) species is evident at pH 2.5 (60%), which gradually increases up to its maximum concentration (80%) at pH 3.5 and thereafter remains constant from pH 3.5 to 5.0.

Besides Pb(II) : L : Be(II) ternary complex species are found to exist in the present system.

(1) Protonated Ligand Species

H₃L: - As the concentration of ternary complex and binary complex increase, the concentration of protonated ligand species H₃L and H₂L are found to exist in decreasing order. The concentration of H₃L species is maximum (36%) at pH 2.5 and declines up to negligible (<1%) at pH 4.0. However H₂L species is identifiable in traces.

(2) Binary Complex Species

Only Pb(II) : L complex has been detected in the Pb(II) : L : Be(II) system whose minimum concentration (5%) is at pH 2.5 and exceeds up to (30%) due to gradual increases in its concentration till pH 5.60, the concentration of ternary & binary complex species are appreciable.

(3) Hydroxo Species

hydroxo species of secondary metal BeOH⁺ and Be(OH)₂ are found to exist from pH 4.25 and 5.0 respectively and their concentration is very small.

(4) Free Metal Ions

The species distribution shows that the primary metal Pb^{2+} and secondary metal Be^{2+} as free metal ions are present in decreasing order of their concentration with incline in the concentration of binary and ternary complexes. The maximum concentration of primary free metal ion (Pb^{2+}) is (36%) which gradually decreases up to negligible in the entire pH range of 2.5 to 4.0. Similarly the maximum concentration of secondary free metal ion (Be^{2+}) is ($\approx 41\%$) at pH 2.5, which gradually decreases up to 20% till pH 4.15.

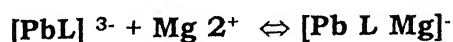
Pb (II) -DTPA-Mg (II) (1:1:1) system:

The species distribution curves are shown in Fig5.16. Proton ligand formations constant for DTPA are given in Table 5.9. DTPA shows five replaceable protons. The proton-ligand formation constants reported here in agree with the earlier reported values (or literature values).

Metal- ligand formation constats

The pH titration curve Fig5.8 and species distribution curve Fig. 5.16 of this ternary systems indicates that Pb(II)-DTPA-Mg (II) type of ternary species is present.

Speciation curves indicate the formation of (1:1:1) ternary complex in the pH range 2.5 to 3.5 according to equilibrium



Minimum concentration of Pb (II)-L-Mg (II) species is evident at pH 2.5 (70%) which gradually increases up to its maximum concentration (80%) at pH 3.5 and there after remains constants from pH 3.5 to 5.0.

Besides Pb (II) -L -Mg (II) ternary complex species are found to exist in the present system

(1) Protonated Ligand Species

H₃L: - The concentration of protonated ligand species H₃L is found to exist in decreasing order. The concentration of H₃L species is maximum (20%) at pH 2.5 and declines up to negligible. H₂L & HL species are found to exist in small amounts

(2) Binary Complex Species

Only Pb (II)-L complex has been detected in the Pb(II)-L-Mg(II) system whose minimum concentration (9%) is at pH 2.5 and exceeds up to (20%) due to gradual increases in its concentration till pH 4.5, the concentration of ternary & binary complex species are appreciable

(3) Hydroxo Species

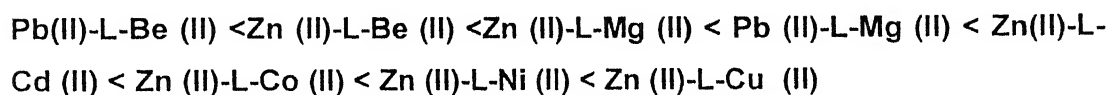
In this system Pb(II)-DTPA-Mg(II), hydroxo species does not appear

(4) Free Metal Ions

The species distribution curves show that the primary metal Pb²⁺ and secondary metal Mg²⁺ as free metal ions are present in decreasing order of their concentration with increase in the concentration of binary and ternary complexes. The maximum concentration of primary free metal ion (Pb²⁺) is (20%) which gradually decreases up to negligible concentration in the entire pH range of 2.5 to 4.0. Similarly the maximum concentration of secondary free metal ion (Mg²⁺) is (30%) at pH 2.5, which gradually decreases up to 20% till pH 4.5

Conclusion Remarks

DTPA serves as an octadentate ligand as it has eight atoms (five oxygen and three nitrogen atoms) through which, it can bind with the metal ions. The octadentate nature of DTPA in its complex was confirmed by the infrared spectral studies by Busch and Bailor. The ionization equilibria are characterized by the following values for the equilibrium constants expressed as their pK values i.e. $pK_1=27.68$, $pK_2=25.86$, $pK_3=23.21$, $pK_4=18.9$ and $pK_5=10.45$. Summation of all the pK values indicates the overall stability constant ($\log \beta$) of the heterobimetallic complexes with DTPA have been presented in Table 5.19. The stability constants of $Mg(II)$ -DTPA- $M(II)$ systems fall in the following orders:



$H_3Zn(II)$ -DTPA complex is expected to involve four coordinate tetrahedral arrangements of coordinate bonds the around $Zn(II)$ metal ion⁽¹⁹⁸⁾. In the complex $Zn(II)$ -DTPA, the $Zn(II)$ is expected to bound two amino-nitrogen. It has still three vacant coordination sites available for interaction with another metal ion and thus making the formation of heterobinuclear complex with DTPA.

In all the mixed metal systems. It has been observed that there is a simultaneous process of complex formation i.e. binary and ternary complexes are formed right from the very beginning of the titration. Hydroxo species are not showing existence in all the ternary system except in $Zn(II)$ -DTPA- $Be(II)$ and $Pb(II)$ -DTPA- $Be(II)$ systems, where $Be(OH)^+$ and $Be(OH)_2$ hydroxo species are identifiable in small amounts at high pH region ($pH > 5.0$). The distribution curves show that hydrolytic equilibria of Be^{2+} aq. ion parallel the buffer region corresponding to metal ligand formation equilibria of ternary complexes.

The proposed structures of these mixed metal chelates seem to be convincing, because stereochemistry of the compound like $Na_2Mg(II)$ EDTA,

H₂O, Ba(II)-Cu(II)-EDTA, 5 H₂O have already been established and are reported in the literature ⁽¹⁹⁹⁾ In case of Zn (II)-DTPA-Co (II), Zn (II)-DTPA-Ni (II), Zn (II)-DTPA-Cu (II), Zn (II)-DTPA-Cd (II), Zn (II)-DTPA-Be (II), Zn (II)-DTPA-Mg (II), Pb (II)-DTPA-Be (II) and Pb (II)-DTPA-Mg (II) systems, for the secondary metal ions Co(II), Ni(II), Cu(II), Cd(II), Be(II) and Mg(II) the tetrahedral and octahedral stereochemistry is well established ⁽²⁰⁰⁾

Table 5.1

Zn (II) -DTPA Co(II) System

- A.** 5 ml NaNO_3 (1 M) + 5 ml HNO_3 (0.02 M) + 40 ml H_2O
- B.** 5 ml NaNO_3 (1 M) + 5 ml HNO_3 (0.02 M) + 5 ml DTPA (0.01 M) + 35 ml H_2O
- C.** 5 ml NaNO_3 (1 M) + 5 ml HNO_3 (0.02 M) + 5 ml DTPA (0.01 M) + 5 ml Zn (II) (0.01 M) + 30 ml H_2O
- D.** 5 ml NaNO_3 (1 M) + 5 ml HNO_3 (0.02 M) + 5 ml DTPA (0.01 M) + 5 ml Zn (II) (0.01 M) + 5 ml Co (II) (0.01M) + 25 ml H_2O

Overall strength of acid = 0.002 M HNO_3

Overall strength of Ligand = 0.001 M DTPA

Overall strength of Zn (II) = 0.001 M

Overall strength of Co (II) = 0.001 M

Ionic Strength = 0.1 M NaNO_3

Strength of Alkali = 0.1 M NaOH

A		B		C		D	
Volume of NaOH ml	pH	Volume of NaOH ml	pH	Volume of NaOH ml.	pH	Volume of NaOH ml	pH
0 0	2.55	0.0	2 79	0 0	2 60	0.0	2 27
0 2	2 63	0.2	2 90	0.2	2 63	0 2	2 32
0 4	2.78	0 4	3 01	0.4	2.67	0 4	2 36
0 6	2 91	0 6	3 15	0 6	2 72	0 6	2 42
0 8	3 20	0 8	3.39	0 8	2 77	0 8	2 48
1 0	4 45	1 0	3.75	1 0	2 84	1.0	2.54
1 2	10 09	1 2	4 21	1.2	2.91	1 2	2.62
1 4	10 49	1 4	5.02	1.4	3 00	1.4	2 71
1 6	10 70	1 6	7.36	1 6	3 10	1 6	2 82
1 8	10 81	1 8	8 33	1 8	3 20	1 8	2 96
2 0	10.92	2 0	8 88	2 0	3 35	2.0	3.12
2 2	11.01	2.2	9 45	2.2	3.51	2.2	3.36
2 4		2 4	9.98	2 4	3.78	2.4	3 69
2 6		2 6	10 26	2 6	4.11	2.6	4 25
2 8		2 8	10 50	2 8	4.65	2 8	7 20
3 0		3.0	10.68	3 0	5 26	3 0	7 62
3 2		3.2	10 80	3 2	8.78	3.2	7 85
3 4		3 4	10.91	3 4	10.04	3 4	7 98
3 6		3.6	11 00	3.6	10.42	3 6	7 98
3 8		3 8	11 07	3.8	10 62	3.8	
4 0		4 0		4.0	10 75	4.0	
4 2		4 2		4.2	10 85	4 2	
4 4		4 4		4.4	10.93	4 4	
4.6				4.6	10 99	4 6	
4 8				4 8	11.05	4.8	
5 0				5 0	11.10	5.0	
						5 2	
						5 4	
						5 6	
						5.8	
						6.0	

Table 5.2

Zn (II) –DTPA Ni (II) System

- A.** 5 ml NaNO_3 (1 M) + 5 ml HNO_3 (0.02 M) + 40 ml H_2O
- B.** 5 ml NaNO_3 (1 M) + 5 ml HNO_3 (0.02 M) + 5 ml DTPA (0.01 M) + 35 ml H_2O
- C.** 5 ml NaNO_3 (1 M) + 5 ml HNO_3 (0.02 M) + 5 ml DTPA (0.01 M) + 5 ml Zn (II) (0.01 M) + 30 ml H_2O
- D.** 5 ml NaNO_3 (1 M) + 5 ml HNO_3 (0.02 M) + 5 ml DTPA (0.01 M) + 5 ml Zn (II) (0.01 M) + 5 ml Ni (II) (0.01M) + 25 ml H_2O

Overall strength of acid = 0.002 M HNO_3

Overall strength of Ligand = 0.001 M DTPA

Overall strength of Zn (II) = 0.001 M

Overall strength of Ni (II) = 0.001 M

Ionic Strength = 0.1 M NaNO_3

Strength of Alkali = 0.1 M NaOH

A		B		C		D	
Volume of NaOH ml	pH	Volume of NaOH ml.	pH	Volume of NaOH ml.	pH	Volume of NaOH ml.	pH
0 0	2 55	0 0	2 79	0.0	2.60	0 0	2 27
0 2	2 63	0 2	2.90	0.2	2 63	0 2	2.31
0 4	2 78	0 4	3.01	0 4	2 67	0 4	2.36
0 6	2 91	0.6	3 15	0 6	2.72	0 6	2 41
0 8	3 20	0.8	3 39	0 8	2.77	0.8	2 48
1 0	4 45	1 0	3 75	1 0	2.84	1 0	2.54
1 2	10 09	1.2	4.21	1.2	2.91	1.2	2 62
1 4	10.49	1 4	5 02	1 4	3.00	1 4	2 72
1 6	10 70	1 6	7 36	1 6	3 10	1.6	2 82
1 8	10 81	1 8	8 33	1 8	3.20	1 8	2 97
2 0	10 92	2 0	8 88	2.0	3 35	2 0	3 17
2 2	11 01	2 2	9 45	2.2	3.51	2 2	3 43
2 4		2 4	9 98	2.4	3.78	2.4	3.87
2 6		2 6	10.26	2.6	4.11	2.6	4.66
2 8		2 8	10 50	2.8	4 65	2.8	7.58
3.0		3 0	10 68	3.0	5.26	3 0	7 77
3 2		3 2	10 80	3 2	8.78	3 2	7 89
3 4		3.4	10 91	3 4	10.04	3 4	8 04
3 6		3.6	11.00	3.6	10.42	3.6	8 21
3 8		3 8	11.07	3.8	10.62	3 8	8 41
4 0		4.0		4.0	10.75	4.0	8 61
4.2		4 2		4 2	10.85	4.2	8 90
4 4		4 4		4 4	10.93	4 4	9 58
4 6				4 6	10.99	4.6	10 22
4 8				4 8	11 05	4 8	10.46
5 0				5 0	11.10	5.0	10 65
						5.2	10.75
						5 4	10 86
						5 6	10.95
						5.8	11.01
						6.0	11.06

Table 5.3

Zn (II) -DTPA Cu (II) System

- A.** 5 ml NaNO_3 (1 M) + 5 ml HNO_3 (0.02 M) + 40 ml H_2O
- B.** 5 ml NaNO_3 (1 M) + 5 ml HNO_3 (0.02 M) + 5 ml DTPA (0.01 M) + 35 ml H_2O
- C.** 5 ml NaNO_3 (1 M) + 5 ml HNO_3 (0.02 M) + 5 ml DTPA (0.01 M) + 5 ml Zn (II) (0.01 M) + 30 ml H_2O
- D.** 5 ml NaNO_3 (1 M) + 5 ml HNO_3 (0.02 M) + 5 ml DTPA (0.01 M) + 5 ml Zn (II) (0.01 M) + 5 ml Cu (II) (0.01 M) + 25 ml H_2O

Overall strength of acid = 0.002 M HNO_3

Overall strength of Ligand = 0.001 M DTPA

Overall strength of Zn (II) = 0.001 M

Overall strength of Cu (II) = 0.001 M

Ionic Strength = 0.1 M NaNO_3

Strength of Alkali = 0.1 M NaOH

A		B		C		D	
Volume of NaOH ml	pH	Volume of NaOH ml	pH	Volume of NaOH ml	pH	Volume of NaOH ml	pH
0 0	2 55	0.0	2 79	0 0	2.60	0.0	2.25
0 2	2 63	0 2	2 90	0 2	2 63	0.2	2 30
0 4	2 78	0 4	3 01	0 4	2 67	0 4	2 34
0 6	2.91	0.6	3.15	0 6	2.72	0.6	2 38
0 8	3 20	0 8	3 39	0 8	2.77	0 8	2 44
1 0	4 45	1 0	3 75	1 0	2 84	1 0	2 50
1 2	10 09	1 2	4 21	1.2	2 91	1 2	2 57
1 4	10 49	1 4	5 02	1.4	3 00	1 4	2.66
1 6	10 70	1 6	7 36	1.6	3 10	1 6	2.76
1 8	10.81	1.8	8 33	1.8	3.20	1 8	2.89
2 0	10 92	2 0	8 88	2.0	3 35	2.0	3 03
2 2	11 01	2 2	9.45	2.2	3.51	2.2	3.27
2.4		2 4	9.98	2.4	3.78	2.4	3.61
2 6		2 6	10 26	2 6	4.11	2 6	4.88
2 8		2 8	10 50	2 8	4.65	2 8	7 56
3 0		3 0	10 68	3 0	5 26	3 0	7 69
3 2		3 2	10 80	3 2	8.78	3 2	7 80
3.4		3 4	10 91	3 4	10.04	3 4	7 90
3.6		3.6	11.00	3.6	10.42	3 6	8 04
3.8		3 8	11.07	3 8	10.62	3.8	8 21
4.0		4.0		4 0	10.75	4 0	8 40
4.2		4 2		4 2	10 85	4 2	8 60
4 4		4 4		4 4	10 93	4 4	8 96
4 6				4 6	10.99	4.6	9.74
4 8				4 8	11.05	4.8	10.52
5 0				5 0	11.10	5.0	
						5.2	
						5.4	
						5.6	
						5.8	
						6.0	

Table 5.4

Zn (II) -DTPA Cd (II) System

- A.** 5 ml NaNO₃ (1 M) + 5 ml HNO₃ (0.02 M) + 40 ml H₂O
- B.** 5 ml NaNO₃ (1 M) + 5 ml HNO₃ (0.02 M) + 5 ml DTPA (0.01 M) + 35 ml H₂O
- C.** 5 ml NaNO₃ (1 M) + 5 ml HNO₃ (0.02 M) + 5 ml DTPA (0.01 M) + 5 ml Zn (II) (0.01 M) + 30 ml H₂O
- D.** 5 ml NaNO₃ (1 M) + 5 ml HNO₃ (0.02 M) + 5 ml DTPA (0.01 M) + 5 ml Zn (II) (0.01 M) + 5 ml Cd (II) (0.01M) + 25 ml H₂O

Overall strength of acid = 0.002 M HNO₃

Overall strength of Ligand = 0.001 M DTPA

Overall strength of Zn (II) = 0.001 M

Overall strength of Cd (II) = 0.001 M

Ionic Strength = 0.1 M NaNO₃

Strength of Alkali = 0.1 M NaOH

A		B		C		D	
Volume of NaOH ml	pH	Volume of NaOH ml	pH	Volume of NaOH ml.	pH	Volume of NaOH ml	pH
0 0	2 55	0.0	2 79	0 0	2 60	0 0	2 30
0 2	2 63	0 2	2 90	0.2	2.63	0 2	2 34
0 4	2 78	0 4	3 01	0 4	2.67	0 4	2 38
0 6	2 91	0 6	3 15	0.6	2 72	0 6	2 44
0 8	3 20	0 8	3 39	0 8	2 77	0 8	2 50
1 0	4 45	1 0	3.75	1 0	2 84	1 0	2 58
1 2	10 09	1 2	4.21	1.2	2 91	1 2	2 66
1 4	10 49	1 4	5 02	1 4	3 00	1 4	2 77
1 6	10 70	1 6	7 36	1 6	3.10	1.6	2 91
1.8	10 81	1 8	8 33	1 8	3.20	1.8	3 08
2 0	10 92	2.0	8 88	2 0	3.35	2.0	3.33
2 2	11 01	2 2	9 45	2 2	3 51	2.2	3 71
2 4		2 4	9 98	2 4	3 78	2 4	4 22
2 6		2 6	10 26	2 6	4.11	2 6	6 13
2 8		2 8	10.50	2 8	4 65	2.8	7 82
3 0		3 0	10 68	3.0	5 26	3.0	7 93
3 2		3 2	10 80	3 2	8 78	3 2	8 01
3 4		3 4	10 91	3.4	10 04	3 4	8 09
3 6		3.6	11 00	3 6	10 42	3.6	8.17
3 8		3 8	11 07	3.8	10 62	3 8	8.22
4 0		4 0		4 0	10 75	4.0	8 34
4 2		4 2		4 2	10 85	4 2	8.54
4 4		4 4		4 4	10 93	4.4	9.41
4 6				4 6	10 99	4.6	10 17
4 8				4 8	11 05	4.8	10 47
5 0				5.0	11.10	5.0	10 61
						5 2	10.74
						5 4	10.84
						5 6	10 83
						5 8	10 99
						6.0	11.05

Table 5.5

Zn (II) -DTPA Be(II) System

- A.** 5 ml NaNO_3 (1 M) + 5 ml HNO_3 (0.02 M) + 40 ml H_2O
- B.** 5 ml NaNO_3 (1 M) + 5 ml HNO_3 (0.02 M) + 5 ml DTPA (0.01 M) + 35 ml H_2O
- C.** 5 ml NaNO_3 (1 M) + 5 ml HNO_3 (0.02 M) + 5 ml DTPA (0.01 M) + 5 ml Zn (II) (0.01 M) + 30 ml H_2O
- D.** 5 ml NaNO_3 (1 M) + 5 ml HNO_3 (0.02 M) + 5 ml DTPA (0.01 M) + 5 ml Zn (II) (0.01 M) + 5 ml Be (II) (0.01M) + 25 ml H_2O

Overall strength of acid = 0.002 M HNO_3

Overall strength of Ligand = 0.001 M DTPA

Overall strength of Zn (II) = 0.001 M

Overall strength of Be (II) = 0.001 M

Ionic Strength = 0.1 M NaNO_3

Strength of Alkali = 0.116 M NaOH

A		B		C		D	
Volume of NaOH ml	pH	Volume of NaOH ml	pH	Volume of NaOH ml.	pH	Volume of NaOH ml.	pH
0 0	2 64	0 0	2 79	0 0	2.37	0.0	2.38
0 2	2.75	0 2	2 90	0 2	2 42	0 2	2.43
0 4	2 88	0 4	3.03	0.4	2.46	0 4	2 48
0 6	3 05	0 6	3 22	0 6	2 50	0 6	2 54
0 8	4 15	0 8	3 46	0 8	2 54	0 8	2 61
1 0	9 80	1.0	3 80	1 0	2 61	1.0	2.67
1.2	10.23	1 2	4 35	1 2	2 69	1 2	2 75
1 4	10 43	1 4	5 39	1 4	2 78	1 4	2 84
1 6	10 56	1 6	8 01	1 6	2 88	1 6	2 99
1 8	10 67	1 8	8 66	1 8	2.97	1.8	2 15
2 0	10.75	2 0	9 22	2 0	3 13	2 0	3 50
2 2	10 81	2 2	9 67	2.2	3 35	2.2	3 91
2 4	10 87	2 4	10 00	2 4	3 63	2 4	4 39
2 6	10 92	2 6	10 24	2 6	4.28	2 6	4 69
2 8	10 97	2 8	10 43	2.8	5 21	2.8	5 05
3.0	11 01	3 0	10.57	3.0	6 43	3 0	5 42
3 2		3 2	10 67	3.2	8.51	3.2	5.95
3 4		3.4	1076	3.4	8.94	3 4	6 19
3 6		3 6	10.83	3.6	9.67	3 6	6 34
3 8		3 8	10 89	3.8	10.20	3.8	7 33
4 0		4 0	10 95	4.0	10.44	4 0	8.32
4 2		4.2	11 00	4 2	10.57	4.2	8 73
4 4		4 4	11 04	4.4	10 71	4 4	9 18

Table 5.6

Zn (II) - DTPA Mg (II) System

- A.** 5 ml NaNO_3 (1 M) + 5 ml HNO_3 (0.02 M) + 40 ml H_2O
- B.** 5 ml NaNO_3 (1 M) + 5 ml HNO_3 (0.02 M) + 5 ml DTPA (0.01 M) + 35 ml H_2O
- C.** 5 ml NaNO_3 (1 M) + 5 ml HNO_3 (0.02 M) + 5 ml DTPA (0.01 M) + 5 ml Zn (II) (0.01 M) + 30 ml H_2O
- D.** 5 ml NaNO_3 (1 M) + 5 ml HNO_3 (0.02 M) + 5 ml DTPA (0.01 M) + 5 ml Zn (II) (0.01 M) + 5 ml Mg (II) (0.01M) + 25 ml H_2O

Overall strength of acid = 0.002 M HNO_3

Overall strength of Ligand = 0.001 M DTPA

Overall strength of Zn (II) = 0.001 M

Overall strength of Mg (II) = 0.001 M

Ionic Strength = 0.1 M NaNO_3

Strength of Alkali = 0.116 M NaOH

A		B		C		D	
Volume of NaOH ml	pH	Volume of NaOH ml	pH	Volume of NaOH ml	pH	Volume of NaOH ml	pH
0 0	2 64	0 0	2 79	0 0	2 37	0.0	2 40
0 2	2 75	0.2	2 90	0.2	2.42	0 2	2 45
0 4	2 88	0 4	3 03	0.4	2 46	0 4	2 49
0 6	3 05	0 6	3 22	0.6	2 50	0 6	2 52
0 8	4 15	0 8	3.46	0.8	2 54	0 8	2 56
1 0	9 80	1.0	3.80	1 0	2 61	1 0	2 61
1 2	10 23	1 2	4 35	1.2	2.69	1 2	2.66
1.4	10.43	1.4	5 39	1.4	2.78	1 4	2 72
1 6	10 56	1 6	8 01	1 6	2.88	1 6	2 79
1 8	10 67	1.8	8 66	1 8	2.97	1 8	2.87
2 0	10 75	2 0	9 22	2 0	3.13	2 0	2 97
2 2	10.81	2 2	9.67	2.2	3.35	2 2	3 10
2 4	10 87	2 4	10 00	2 4	3.63	2.4	3.29
2 6	10 92	2 6	10 24	2 6	4 28	2 6	3 56
2 8	10 97	2 8	10.43	2 8	5.21	2 8	3 91
3 0	11 01	3 0	10.57	3.0	6 43	3.0	4.49
3 2		3.2	10.67	3 2	8 51	3.2	5 18
3 4		3.4	1076	3 4	8.94	3.4	6 11
3 6		3 6	10.83	3.6	9 67	3 6	8 35
3 8		3 8	10.89	3 8	10.20	3.8	8 67
4 0		4.0	10.95	4 0	10.44	4.0	9 01
4 2		4.2	11.00	4 2	10 57	4 2	9 74
4.4		4 4	11.04	4.4	10.71	4.4	10 17

Table 5.7

Pb(II) –DTPA Be(II) System

- A.** 5 ml NaNO₃ (1 M) + 5 ml HNO₃ (0.02 M) + 40 ml H₂O
- B.** 5 ml NaNO₃ (1 M) + 5 ml HNO₃ (0.02 M) + 5 ml DTPA (0.01 M) + 35 ml H₂O
- C.** 5 ml NaNO₃ (1 M) + 5 ml HNO₃ (0.02 M) + 5 ml DTPA (0.01 M) + 5 ml Pb (II) (0.01 M) + 30 ml H₂O
- D.** 5 ml NaNO₃ (1 M) + 5 ml HNO₃ (0.02 M) + 5 ml DTPA (0.01 M) + 5 ml Pb (II) (0.01 M) + 5 ml Be (II) (0.01M) + 25 ml H₂O

Overall strength of acid = 0.002 M HNO₃

Overall strength of Ligand = 0.001 M DTPA

Overall strength of Pb (II) = 0.001 M

Overall strength of Be (II) = 0.001 M

Ionic Strength = 0.1 M NaNO₃

Strength of Alkali = 0.116 M NaOH

A		B		C		D	
Volume of NaOH ml	pH	Volume of NaOH ml	pH	Volume of NaOH ml	pH	Volume of NaOH ml	pH
0 0	2 64	0 0	2 79	0.0	2 56	0 0	2 51
0 2	2 75	0 2	2.90	0.2	2 60	0.2	2.56
0 4	2 88	0 4	3 03	0.4	2 65	0 4	2 62
0 6	3 05	0 6	3 22	0.6	2.67	0 6	2 69
0 8	4.15	0 8	3 46	0 8	2 71	0 8	2 76
1 0	9.80	1 0	3.80	1.0	2 76	1 0	2 80
1 2	10 23	1 2	4.35	1.2	2 81	1 2	2 96
1 4	10 43	1 4	5 39	1.4	2 89	1 4	3 09
1 6	10.56	1 6	8.01	1.6	2.97	1 6	3 27
1 8	10 67	1 8	8.66	1.8	3 10	1.8	3 49
2 0	10 75	2 0	9 22	2 0	3 20	2 0	3 80
2 2	10 81	2 2	9 67	2 2	3.35	2 2	4 16
2 4	10 87	2 4	10 00	2.4	3.57	2 4	4 42
2 6	10 92	2 6	10 24	2.6	3.92	2 6	4 64
2 8	10.97	2 8	10.43	2.8	.432	2 8	4 88
3.0	11.01	3 0	10 57	3.0	4.78	3.0	5 15
3.2		3 2	10 67	3.2	5.65	3 2	5 58
3 4		3.4	1076	3.4	9.47	3.4	6 09
3 6		3.6	10.83	3.6	10.19	3.6	6 30
3 8		3.8	10.89	3.8	10.48	3.8	6 76
4 0		4.0	10 95	4.0	10.62	4.0	9.50
4 2		4.2	11.00	4.2	1075	4.2	10.10
4 4		4.4	11 04	4 4	10.83	4.4	10 38

Table 5.8

Pb (II) –DTPA Mg (II) System

- A.** 5 ml NaNO_3 (1 M) + 5 ml HNO_3 (0.02 M) + 40 ml H_2O
- B.** 5 ml NaNO_3 (1 M) + 5 ml HNO_3 (0.02 M) + 5 ml DTPA (0.01 M) + 35 ml H_2O
- C.** 5 ml NaNO_3 (1 M) + 5 ml HNO_3 (0.02 M) + 5 ml DTPA (0.01 M) + 5 ml Pb (II) (0.01 M) + 30 ml H_2O
- D.** 5 ml NaNO_3 (1 M) + 5 ml HNO_3 (0.02 M) + 5 ml DTPA (0.01 M) + 5 ml Pb (II) (0.01 M) + 5 ml Mg (II) (0.01M) + 25 ml H_2O

Overall strength of acid = 0.002 M HNO_3

Overall strength of Ligand = 0.001 M DTPA

Overall strength of Pb (II) = 0.001 M

Overall strength of Mg (II) = 0.001 M

Ionic Strength = 0.1 M NaNO_3

Strength of Alkali = 0.116 M NaOH

A		B		C		D	
Volume of NaOH ml	pH	Volume of NaOH ml	pH	Volume of NaOH ml	pH	Volume of NaOH ml	pH
0 0	2 64	0 0	2.79	0 0	2.56	0.0	2 70
0 2	2.75	0 2	2.90	0 2	2 60	0 2	2 77
0 4	2 88	0 4	3.03	0 4	2.65	0 4	2.84
0 6	3 05	0 6	3 22	0.6	2 67	0 6	2 92
0 8	4 15	0.8	3 46	0.8	2 71	0.8	3.00
1 0	9 80	1.0	3 80	1 0	2.76	1.0	3.09
1.2	10 23	1.2	4.35	1.2	2.81	1 2	3 21
1 4	10 43	1 4	5 39	1.4	2 89	1 4	3 33
1 6	10 56	1 6	8.01	1.6	2.97	1.6	3.49
1 8	10 67	1.8	8 66	1.8	3.10	1 8	3.64
2 0	10 75	2 0	9.22	2.0	3 20	2.0	3 83
2 2	10 81	2.2	9 67	2 2	3 35	2 2	4 05
2 4	10 87	2 4	10 00	2 4	3 57	2 4	4.27
2 6	10 92	2.6	10.24	2 6	3 92	2 6	4 52
2 8	10 97	2 8	10 43	2.8	432	2 8	4 79
3 0	11 01	3 0	10.57	3 0	4.78	3.0	5.12
3 2		3 2	10 67	3 2	5.65	3 2	5 46
3 4		3 4	1076	3 4	9.47	3 4	5 97
3 6		3 6	10 83	3 6	10 19	3 6	6 45
3 8		3.8	10.89	3.8	10.48	3 8	6.67
4 0		4 0	10 95	4 0	10 62	4.0	7 41
4 2		4 2	11.00	4 2	1075	4 2	8 15
4 4		4 4	11.04	4.4	10 83	4.4	9 25

Table 5.9

Proton –Ligand formation constant ($\log \beta_{\text{overall}}$) of DTPA at ± 37
 1°C and $\mu=0.1 \text{ mole dm}^{-3} \text{ NaNO}_3$.

S NO.	Species	p	q	r	s	t	$\log \beta$
(i)	H_5L	0	0	1	0	-5	27.68
(ii)	H_4L	0	0	1	0	-4	25.86
(iii)	H_3L	0	0	1	0	-3	23.21
(iv)	H_2L	0	0	1	0	-2	18.98
(v)	HL	0	0	1	0	-1	10.45

Table 5.10

Hydrolytic constants of Be^{2+} aq. ion

S NO	Species	p	q	r	s	t	$\log \beta$
(i)	$\text{Be}(\text{OH})^+$	1	0	0	0	1	-5.70
(ii)	$\text{Be}(\text{OH})_2$	1	0	0	0	2	-11.16

Table – 5.11

Metal- ligand binary and ternary constants of Zn(II)-DTPA-CO(II) system in aqueous solution at $37 \pm 1^{\circ}$ and $\mu = 0.1 \text{ mol dm}^{-3} \text{ NaNO}_3$

(A) Metal- Ligand formation constants: Binary system						
Species	p	q	r	s	t	log β
Zn-L	1	0	1	0	0	18 23
CO-L	0	1	1	0	0	19 08
(B) Metal- Ligand formation constants: Ternary system						
Zn-L-CO	1	1	1	0	0	21.95

Table – 5.12

Metal- ligand binary and ternary constants of Zn(II)-DTPA-Ni(II) system in aqueous solution at $37 \pm 1^{\circ}$ and $\mu = 0.1 \text{ mol dm}^{-3} \text{ NaNO}_3$

(A) Metal- Ligand formation constants: Binary system						
Species	p	q	r	s	t	log β
Zn-L	1	0	1	0	0	18 23
Ni-L	0	1	1	0	0	20 11
(B) Metal- Ligand formation constants: Ternary system						
Zn-L-Ni	1	1	1	0	0	23 82

Table – 5.13

Metal– ligand binary and ternary constants of Zn(II)–DTPA–Cu(II) system
in aqueous solution at $37 \pm 1^{\circ}$ and $\mu = 0.1 \text{ mol dm}^{-3} \text{ NaNO}_3$

(A) Metal- Ligand formation constants: Binary system						
Species	p	q	r	s	t	log β
Zn-L	1	0	1	0	0	18.23
Cu-L	0	1	1	0	0	21.29
(B) Metal- Ligand formation constants: Ternary system						
Zn-L -Cu	1	1	1	0	0	24.98

Table – 5.14

Metal– ligand binary and ternary constants of Zn(II)–DTPA–Cd(II) system
in aqueous solution at $37 \pm 1^{\circ}$ and $\mu = 0.1 \text{ mol dm}^{-3} \text{ NaNO}_3$

(A) Metal- Ligand formation constants: Binary system						
Species	p	q	r	s	t	log β
Zn-L	1	0	1	0	0	18.23
Cd-L	0	1	1	0	0	18.95
(B) Metal- Ligand formation constants: Ternary system						
Zn-L -Cd	1	1	1	0	0	20.53

Table – 5.15

Metal– ligand binary and ternary constants of Zn(II)–DTPA–Be(II) system in aqueous solution at $37 \pm 1^{\circ}$ and $\mu = 0.1 \text{ mol dm}^{-3} \text{ NaNO}_3$

(A) Hydrolytic constants of Be²⁺ (II) aq. Ion.						
Species	p	q	r	s	t	log β
Be (OH) ⁺	0	1	0	0	1	-5.7
Be (OH) ₂	0	1	0	0	2	-11.5
(B) Metal- Ligand formation constants: Binary system						
Zn-L	1	0	1	0	0	18.23
Be-L	0	1	1	0	0	8.53
(C) Metal- Ligand formation constants: Ternary system						
Zn-L -Be	1	1	1	0	0	19.38

Table – 5.16

Metal– ligand binary and ternary constants of Zn(II)–DTPA–Mg(II) system in aqueous solution at $37 \pm 1^{\circ}$ and $\mu = 0.1 \text{ mol dm}^{-3} \text{ NaNO}_3$

(A) Metal- Ligand formation constants: Binary system						
Species	p	q	r	s	t	log β
Zn-L	1	0	1	0	0	18.23
Mg-L	0	1	1	0	0	9.31
(B) Metal- Ligand formation constants: Ternary system						
Zn-L -Mg	1	1	1	0	0	19.83

Table – 5.17

Metal– ligand binary and ternary constants of Pb(II)–DTPA–Be(II) system in aqueous solution at $37 \pm 1^{\circ}$ and $\mu = 0.1 \text{ mol dm}^{-3} \text{ NaNO}_3$

(A) Hydrolytic constants of Be²⁺ (II) aq. Ion.						
Species	p	q	r	s	t	log β
Be (OH) ⁺	0	1	0	0	1	-5.7
Be (OH) ₂	0	1	0	0	2	-11.5
(B) Metal- Ligand formation constants: Binary system						
Pb-L	1	0	1	0	0	18.53
Be-L	0	1	1	0	0	8.53
(C) Metal- Ligand formation constants: Ternary system						
Pb-L -Be	1	1	1	0	0	19.13

Table – 5.18

Metal– ligand binary and ternary constants of Pb(II)–DTPA–Mg(II) system in aqueous solution at $37 \pm 1^{\circ}$ and $\mu = 0.1 \text{ mol dm}^{-3} \text{ NaNO}_3$

(A) Metal- Ligand formation constants: Binary system						
Species	p	q	r	s	t	log β
Pb-L	1	0	1	0	0	18.53
Mg-L	0	1	1	0	0	9.31
(B) Metal- Ligand formation constants: Ternary system						
Pb-L -Mg	1	1	1	0	0	20.13

Table 5.19

Stability constant values for the mixed metal-complexes of DTPA at $37 \pm 1^\circ$ and $\mu = 0.1 \text{ mol dm}^{-3}$ (NaNO₃)	
Reaction	$\log \beta_{11100}$
$\text{Zn}^{2+} + \text{DTPA}^{5-} + \text{Co}^{2+} \rightleftharpoons [\text{Zn} - \text{DTPA-Co}]^-$	21.95
$\text{Zn}^{2+} + \text{DTPA}^{5-} + \text{Ni}^{2+} \rightleftharpoons [\text{Zn} - \text{DTPA-Ni}]^-$	23.82
$\text{Zn}^{2+} + \text{DTPA}^{5-} + \text{Cu}^{2+} \rightleftharpoons [\text{Zn} - \text{DTPA-Cu}]^-$	24.98
$\text{Zn}^{2+} + \text{DTPA}^{5-} + \text{Cd}^{2+} \rightleftharpoons [\text{Zn} - \text{DTPA-Cd}]^-$	20.53
$\text{Zn}^{2+} + \text{DTPA}^{5-} + \text{Be}^{2+} \rightleftharpoons [\text{Zn} - \text{DTPA-Be}]^-$	19.38
$\text{Zn}^{2+} + \text{DTPA}^{5-} + \text{Mg}^{2+} \rightleftharpoons [\text{Zn} - \text{DTPA-Mg}]^-$	19.83
$\text{Pb}^{2+} + \text{DTPA}^{5-} + \text{Be}^{2+} \rightleftharpoons [\text{Pb} - \text{DTPA-Be}]^-$	19.13
$\text{Pb}^{2+} + \text{DTPA}^{5-} + \text{Mg}^{2+} \rightleftharpoons [\text{Pb} - \text{DTPA-Mg}]^-$	20.13

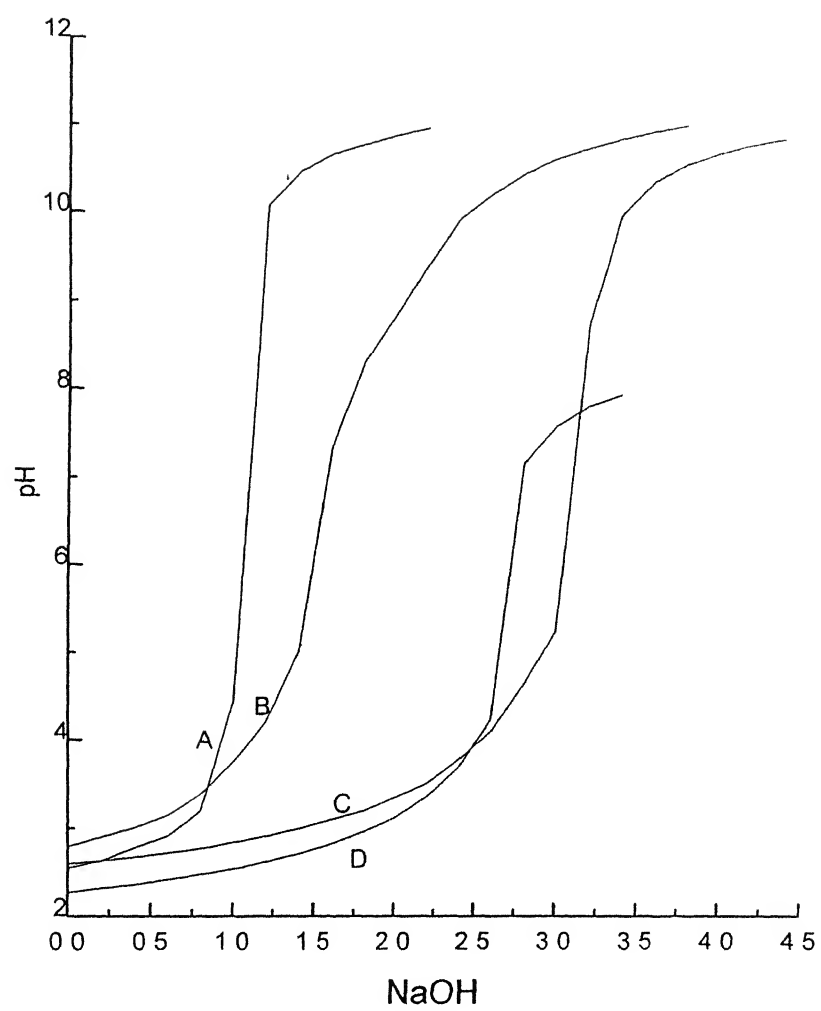


Fig 5 1 Titration curves of Zn[II]-DTPA-Co[II] System

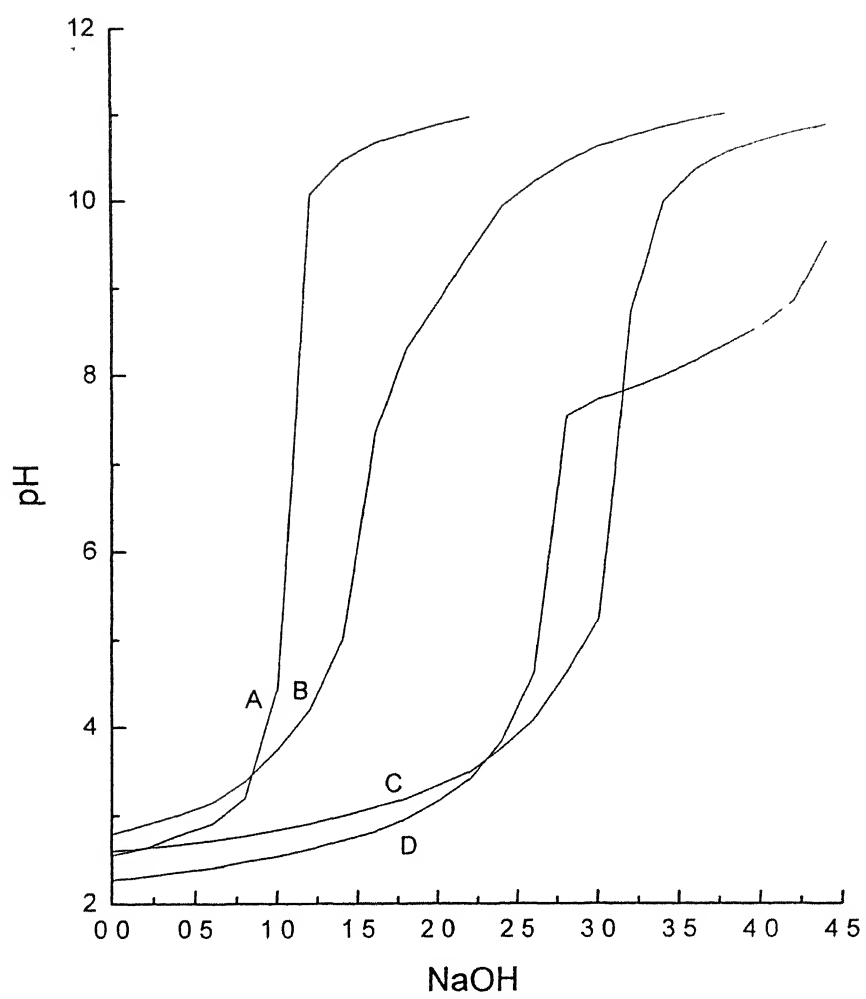


Fig 5 2 Titration curves of Zn[II]-DTPA-Ni[II] System

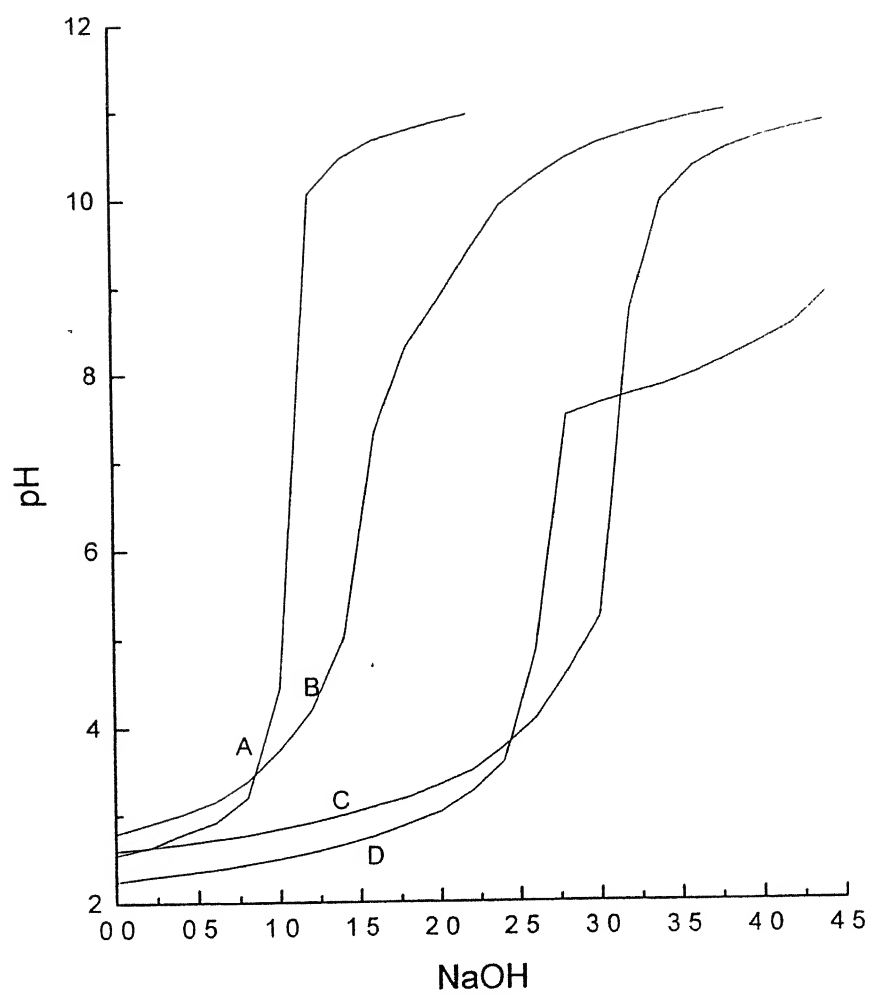


Fig 5 3 Titration curves of Zn[II]-DTPA-Cu[II] System

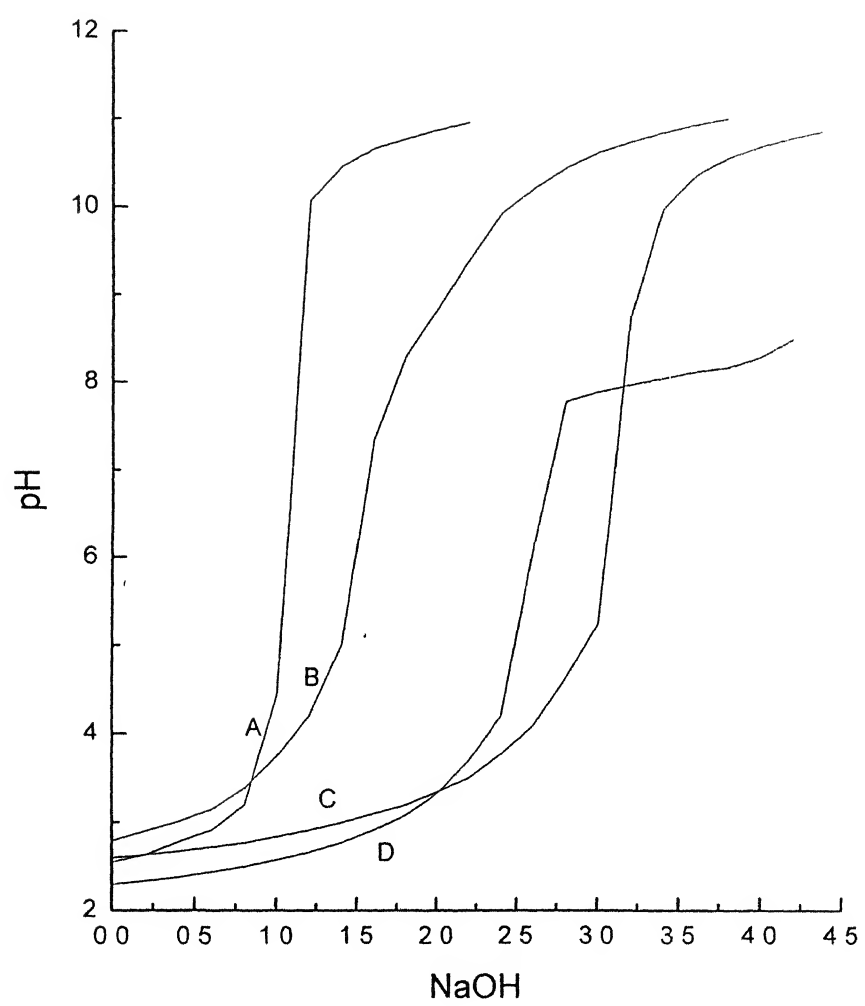


Fig 5 4 Titration curves of Zn[II]-DTPA-Cd[II] System

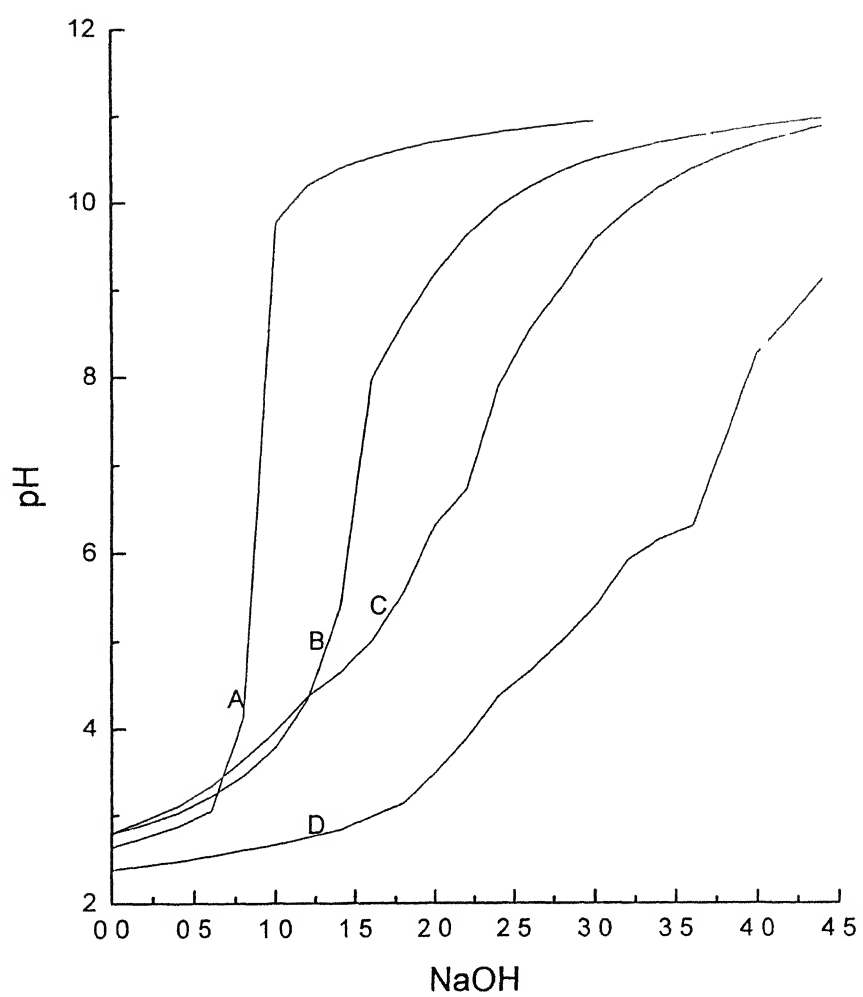


Fig. 5.5 Titration curves of Zn(II)-DTPA-Be(II) System.

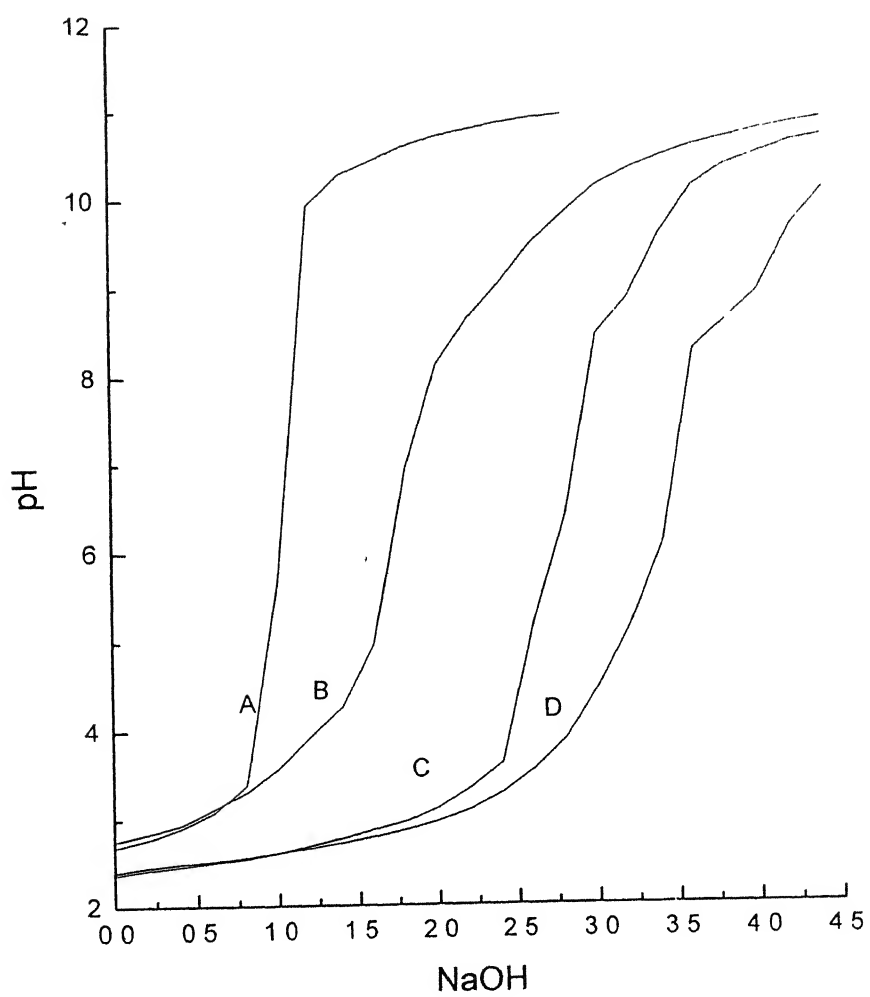


Fig. 5.6 Titration curves of Zn(II)-DTPA-Mg(II) System.

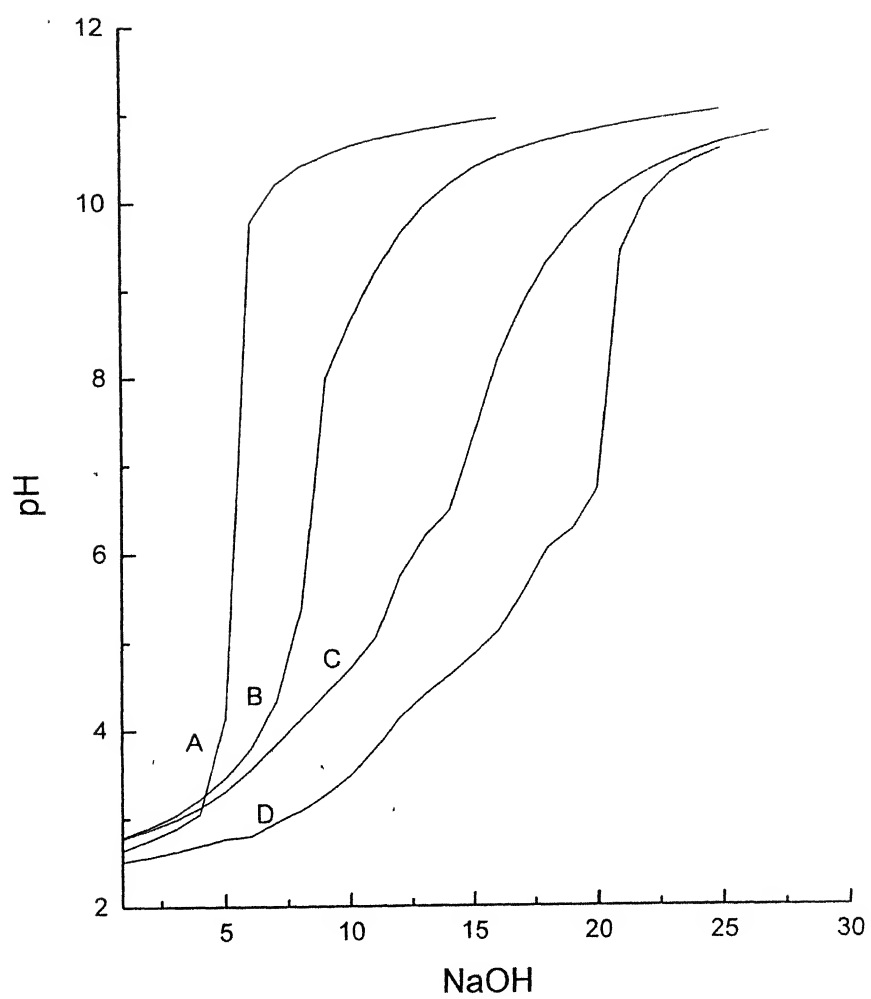


Fig.5.7 Titration curves of Pb(II)-DTPA-Be(II) System.

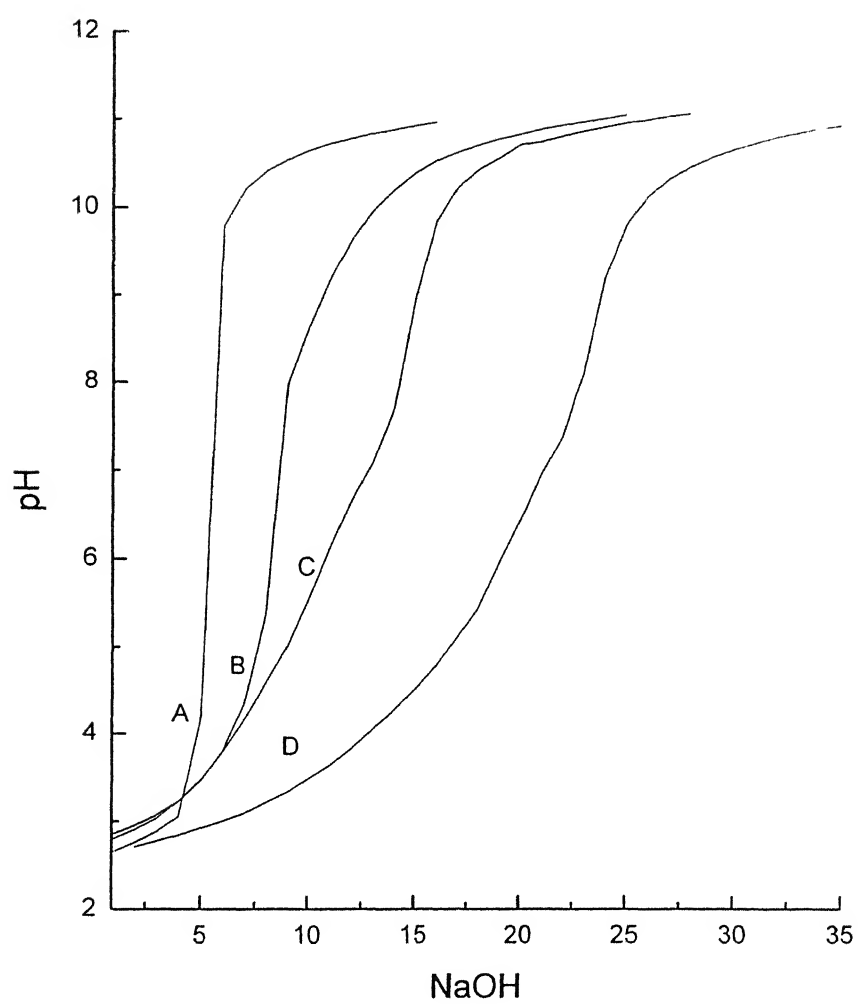


Fig. 5.8 Titration curves of Pb(II)-DTPA-Mg(II) System.

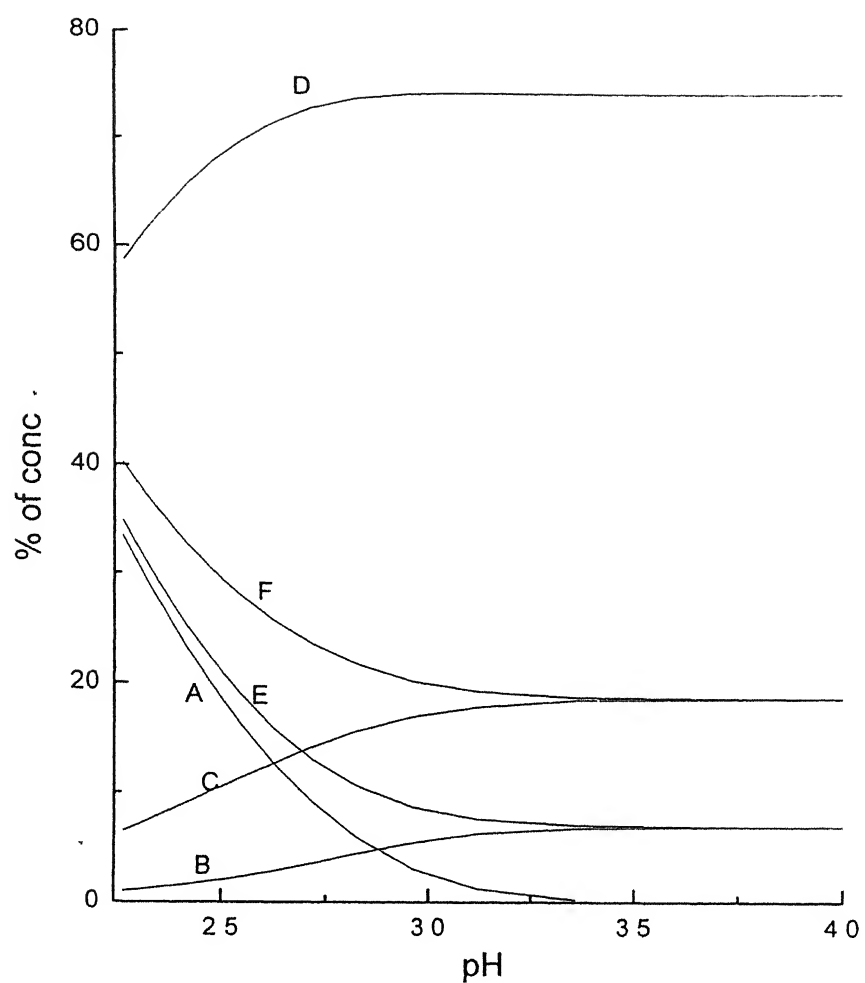


Fig 5.9 Species distribution curve of Zn(II)-DTPA-Co(II) System
 Where (A) H L (B) Zn(II)-DTPA (C) Co(II)-DTPA (D) Zn(II)-DTPA-Co(II)
 (E) Zn(II) (F) Co(II)

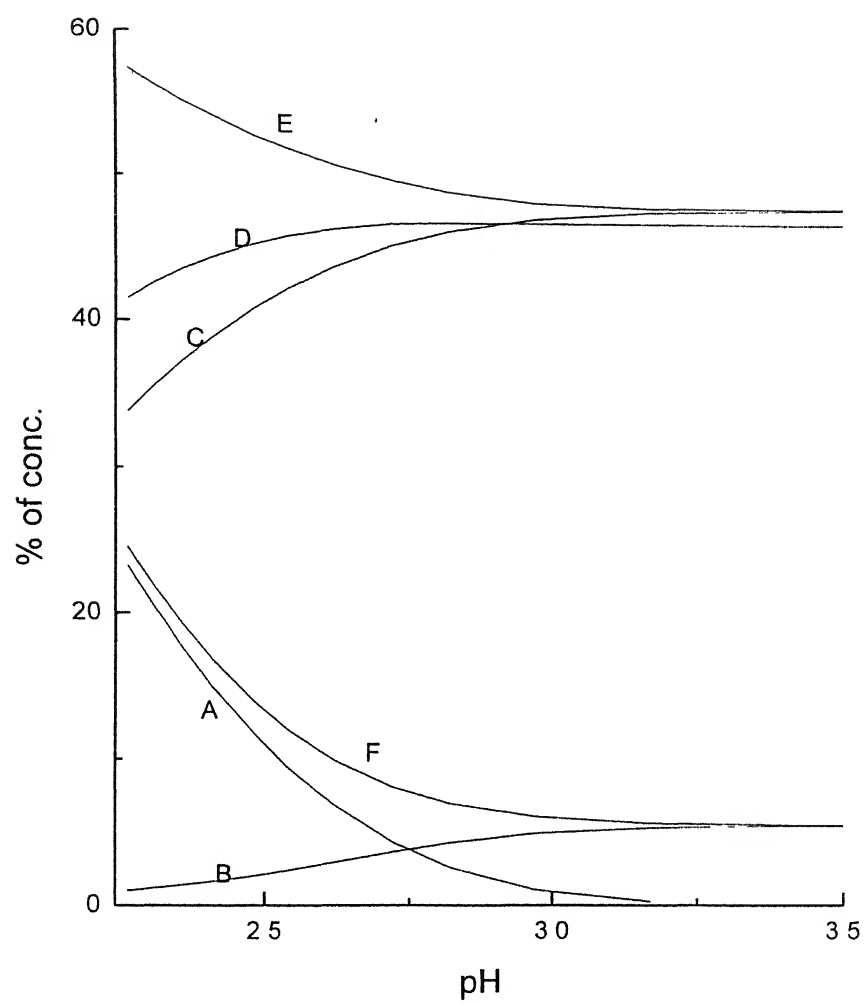


Fig 5 10 Species distribution curve of Zn(II)-DTPA-Ni(II) System
Where (A) H L (B) Zn(II)-DTPA (C) Ni(II)-DTPA (D) Zn(II)-DTPA-Ni(II)
(E) Zn(II) (F) Ni(II)

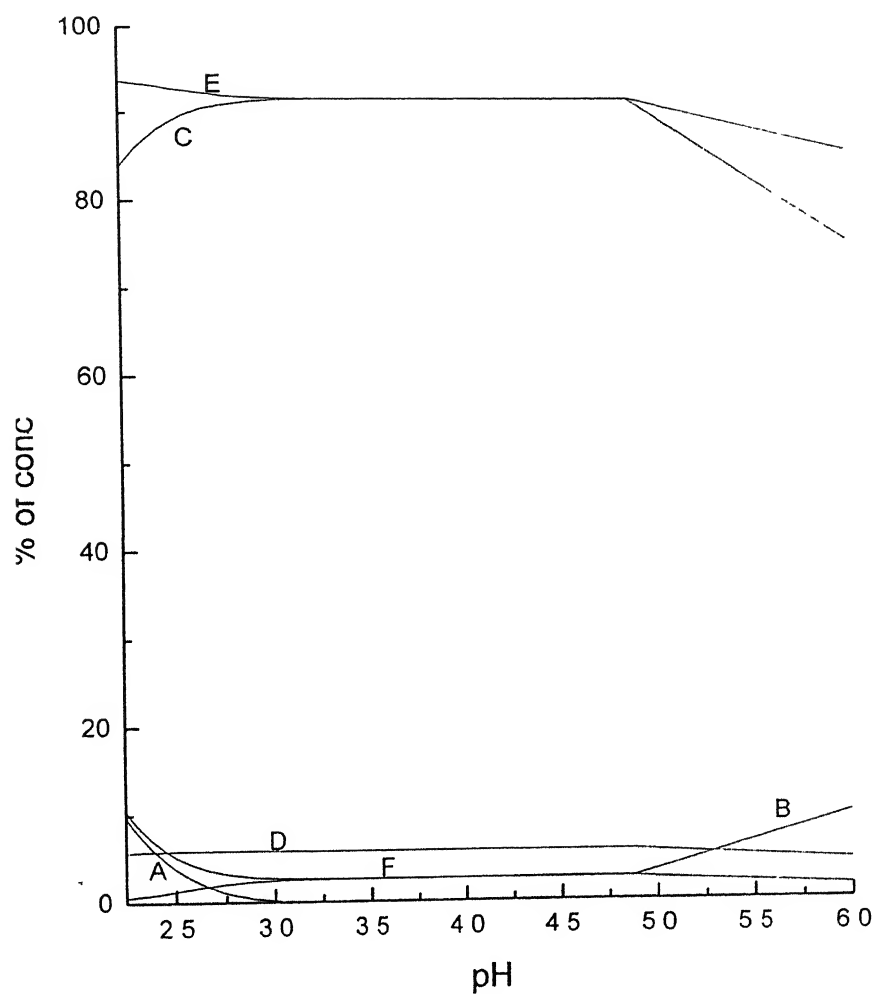


Fig. 5.11 Species distribution curve of Zn(II)-DTPA-Cu(II) System
 Where (A) H⁺ (B) Zn(II)-DTPA (C) Cu(II)-DTPA (D) Zn(II)-DTPA-Cu(II)
 (E) Zn(II) (F) Cu(II)

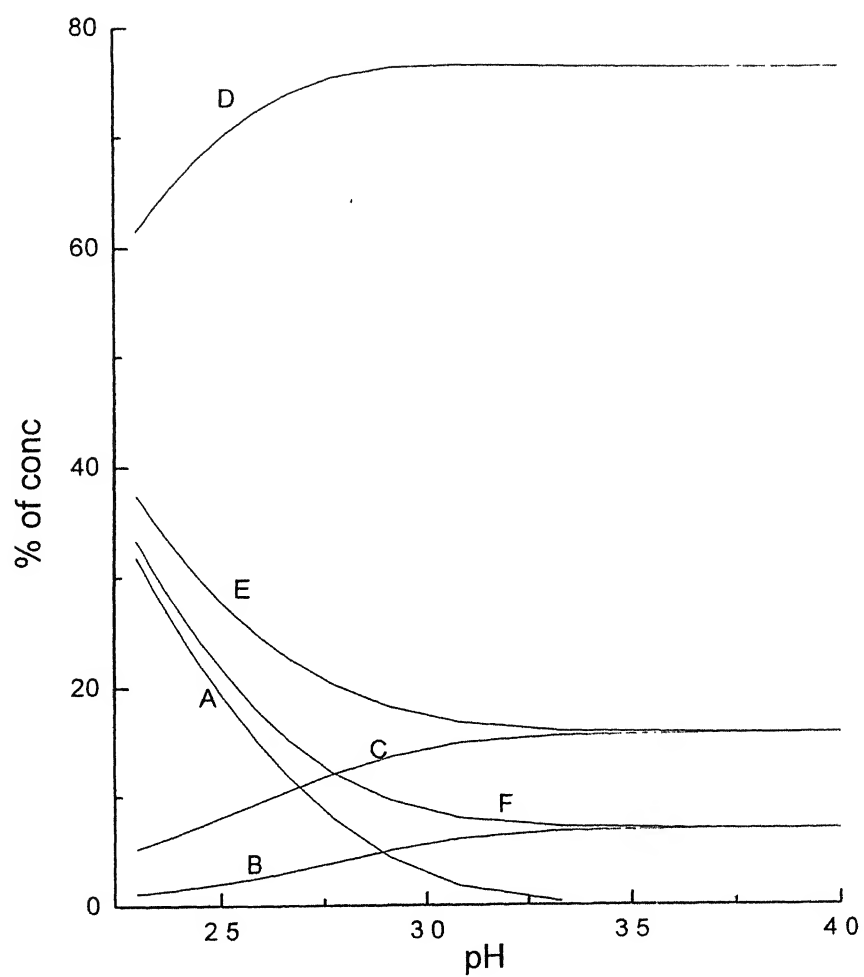


Fig 5 12 Species distribution curve of Zn(II)-DTPA- Cd(II) System where (A) H⁺ (B) Zn(II)-DTPA (C) Cd(II)-DTPA (D) Zn(II)-DTPA-Cd(II) (E) Zn(II) (F) Cd(II)

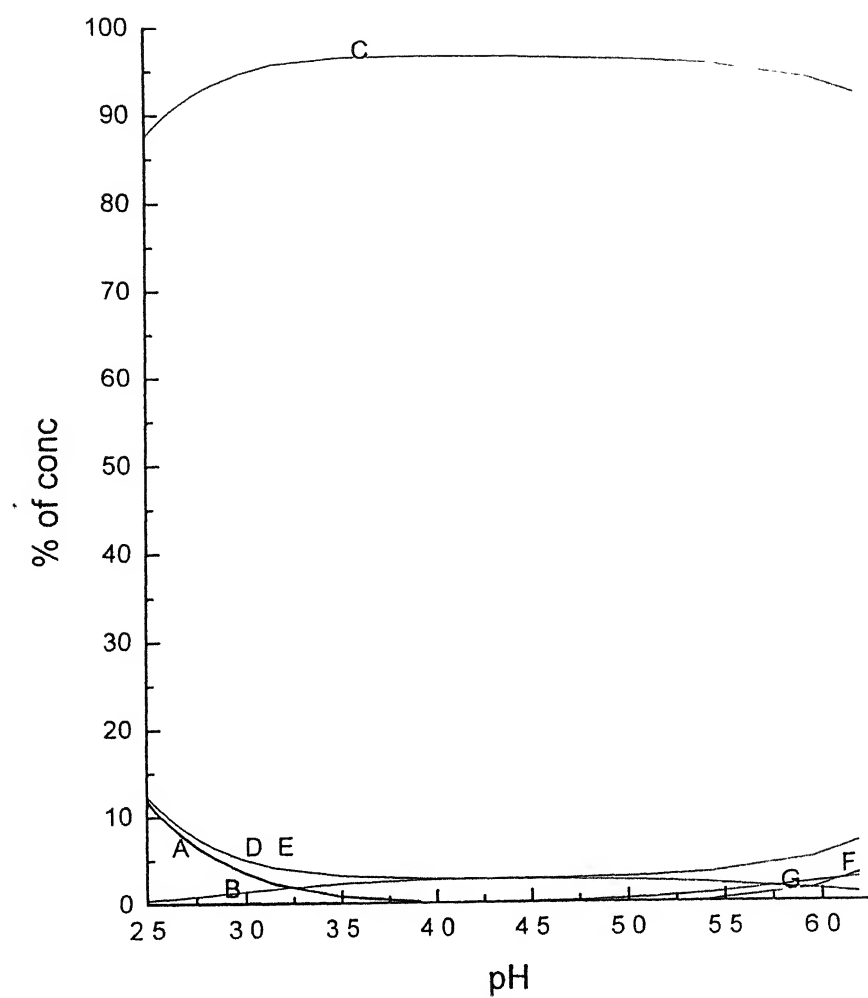


Fig 5 13 Species distribution curve of Zn(II)-DTPA-Be(II) System
Where (A) H L (B) Zn(II)-DTPA (C) Zn(II)-DTPA-Be(II) (D) Zn(II)
(E) Be(II) (F) Be(OH)+ (G) B(OH)2

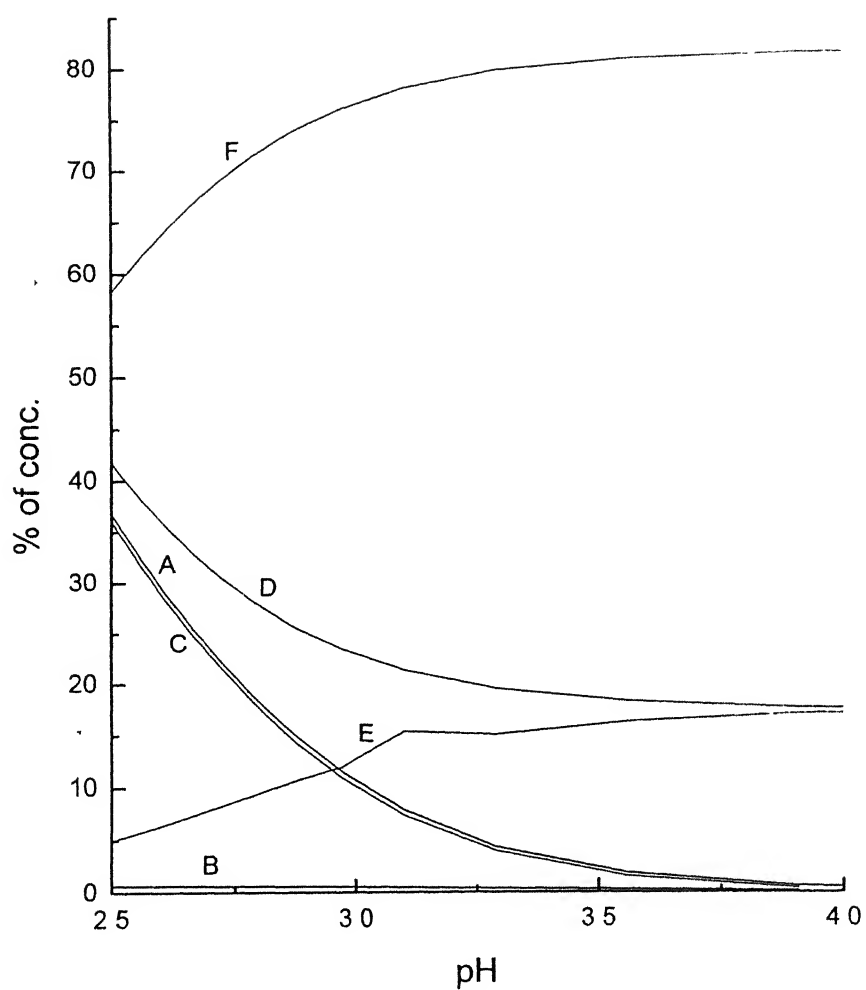


Fig. 5.14 Species distribution curves of Zn(II)-DTPA-Mg(II) System
 Where (A) H⁺ (B) H⁺ (C) Zn(II) (D) Mg(II) (E) Zn(II)-DTPA
 (F) Zn(II)-DTPA-Mg(II).

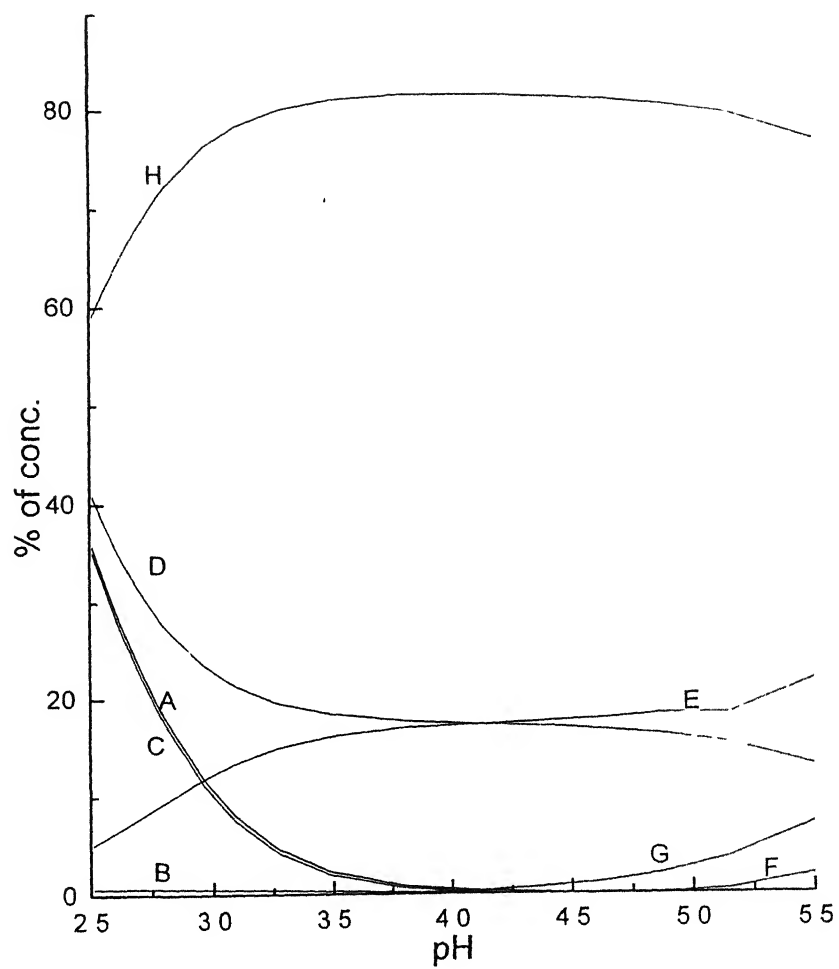


Fig 5 15 Species distribution curves of Pb(II)-DTPA-Be(II) System
 Where (A) H L (B)H L (C) Pb(II) (D) Be(II) (E) Pb(II)-DTPA
 (F) Be(OH)+ (G) Be(OH)2 (H) Pb(II)-DTPA-Be(II)

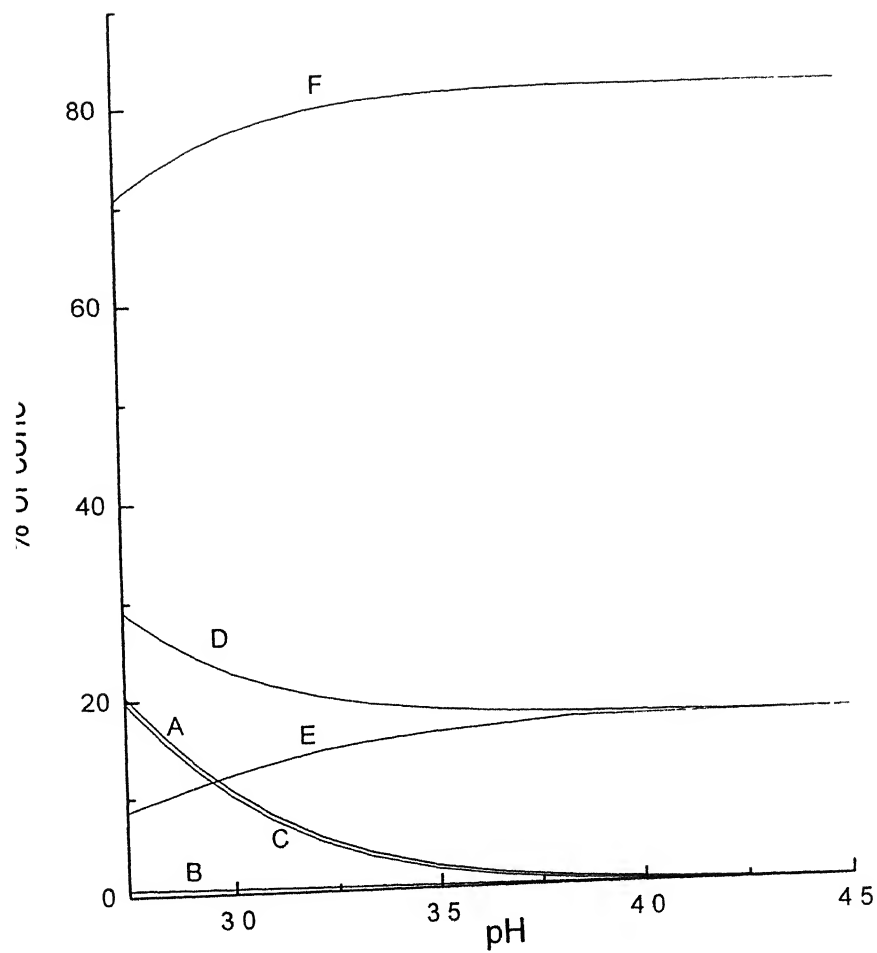


Fig.5.16 Species distribution curve of Pb(II)-DTPA-Mg(II) System
 Where (A) H L (B) H L (C) Pb(II) (D) Mg(II) (E) Pb(II)-DTPA
 (F) Pb(II)-DTPA-Mg(II).

STRUCTURAL ASPECTS:

The stereochemistry of DTPA chelates is quite similar to that of EDTA chelates. The solution structure of DTPA is shown in Fig

The proton dissociation of $\text{Na}_2\text{H}_3\text{DTPA}$ can be expressed as

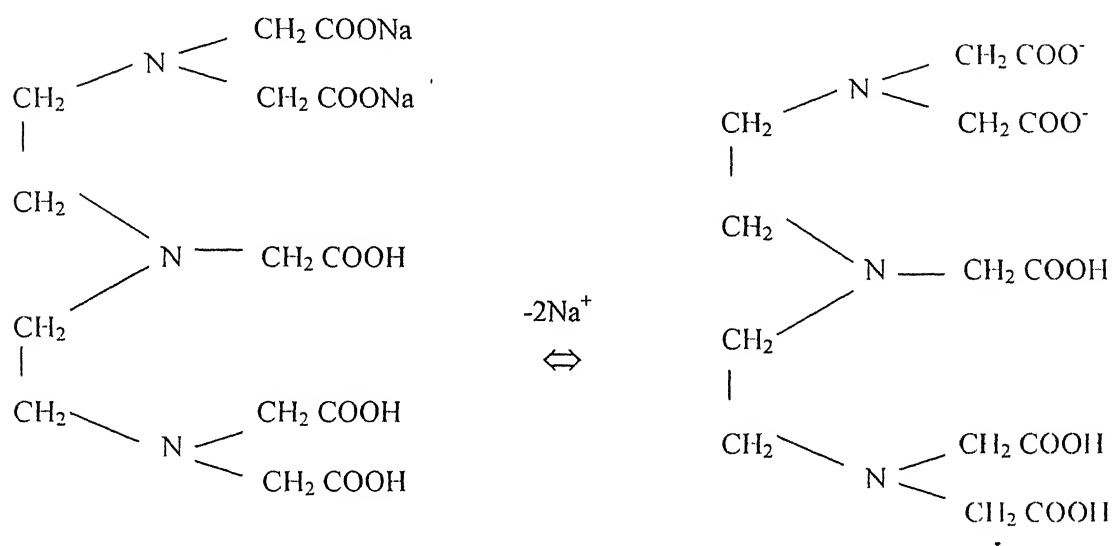


Fig. 1 Structure of Ionic Dissociation of Disodium Salt of DTPA

This protonated form of the ligand forms a stable complex with Zn (II) and Pb(II) metal ions

Distribution profiles of the binary and ternary complexes suggested the formation of binary and ternary complexes by coordination of ligand with the metal ions. As in binary complex Zn (II) blocked 4 coordination sites, giving the ~~tetrahedral~~ tetrahedral geometry due to Jahn-Teller effect, leaving two sites uncoordinated. Pb(II) blocked four coordination sites of this ligand leaving four uncoordinated sites.

The $\log \beta$ values of Zn (II) –DTPA and Pb(II) –DTPA are 18.29 and 18.66 respectively, as reported in the literature and is also found nearly the same by the $\log \beta$ values under present experimental condition. The reported values of stability constants of alkaline earth metal complexes with DTPA are $10^6 - 10^8$ times, less than the $\log k$ values of Zn (II)-DTPA and Pb (II)- DTPA. So Zn (II) and Pb (II) form stronger complexes with DTPA. When the alkaline earth metals are introduced into the solution as second metal, it gets attached to the remaining vacant coordination sites of the ligand forming the mixed metal complexes. On the basis of stability constant, the analytical data, and IR spectral data the most probable structure of chelates are shown in Fig.

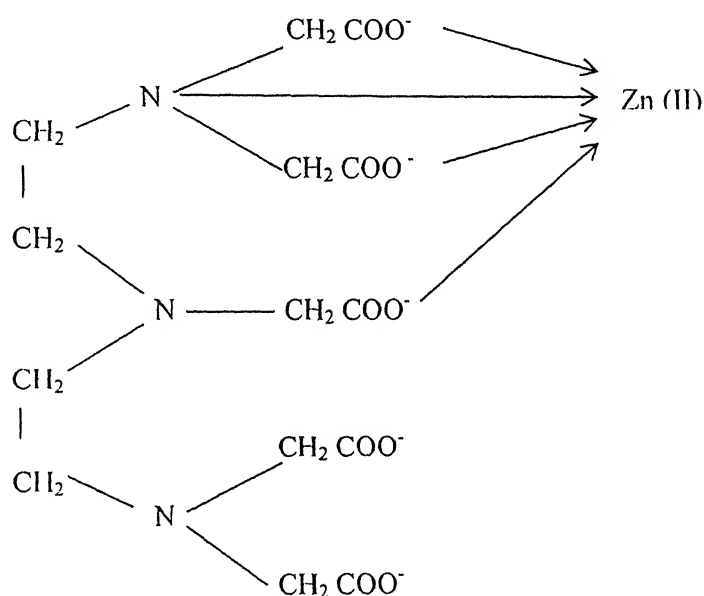


Fig. 2 Proposed Structure of Zn (II) –DTPA complex

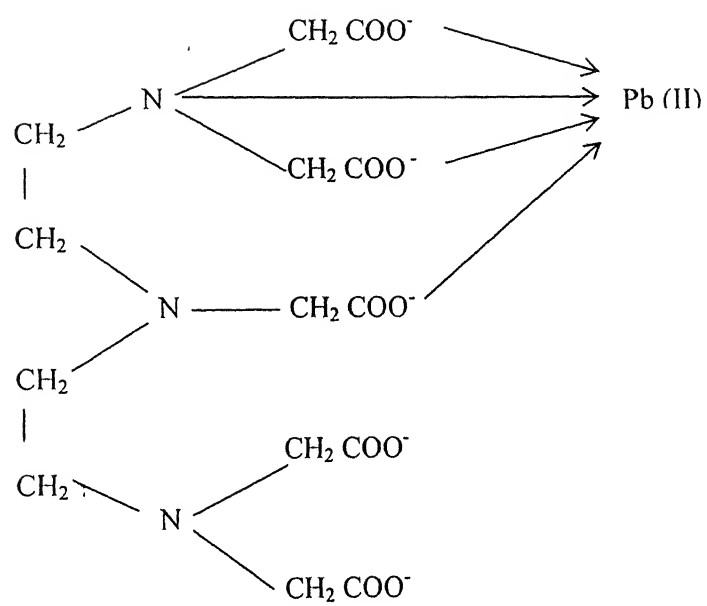


Fig. 3 Proposed Structure of Pb (II) –DTPA complex

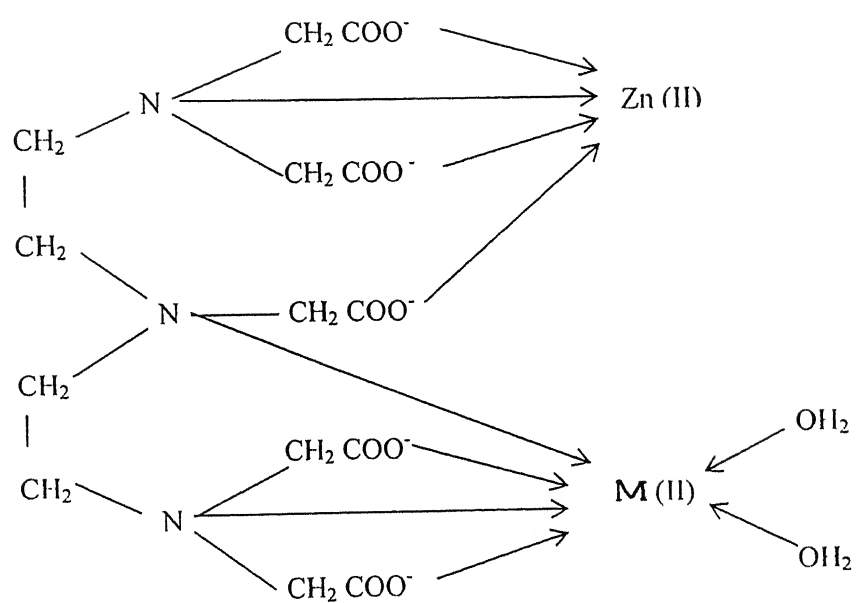


Fig. 4 Proposed Structure of Zn (II) –DTPA-M (II) complex
Where M (II) stands for Mg(II), Co(II), Ni(II), Cu(II).

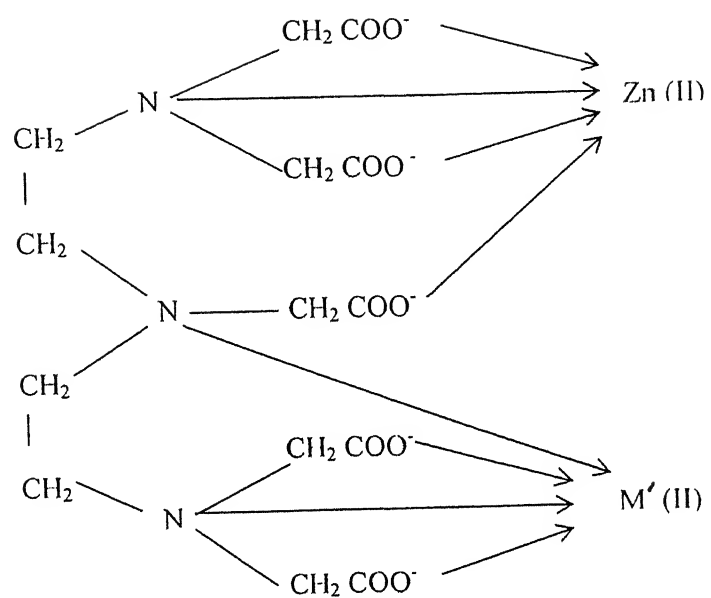


Fig. 5 Proposed Structure of Zn (II) –DTPA-M' (II) complex
Where M' (II) stands for Be (II), Cd (II).

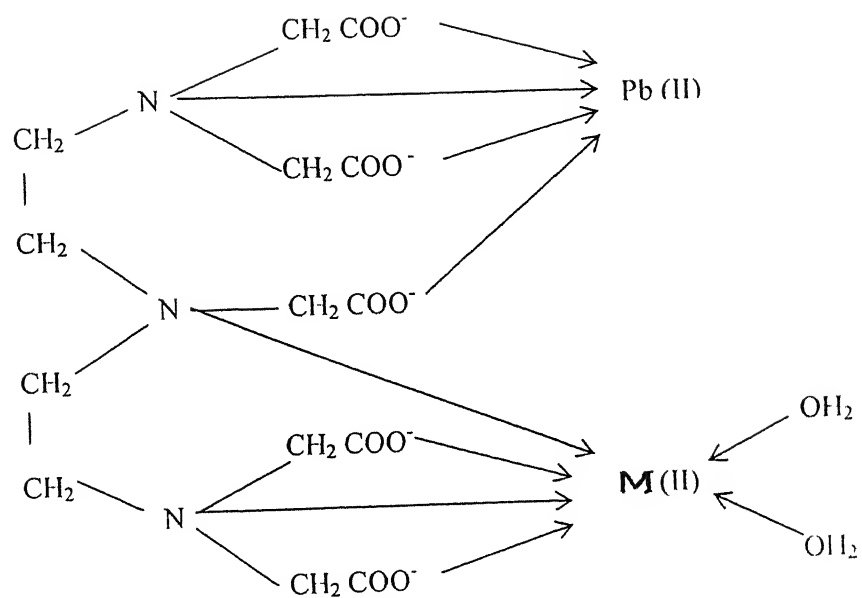


Fig. 6 Proposed Structure of Pb (II) –DTPA-M (II) complex
 Where $M(II) = Mg(II), Co(II), Ni(II), Cu(II)$.

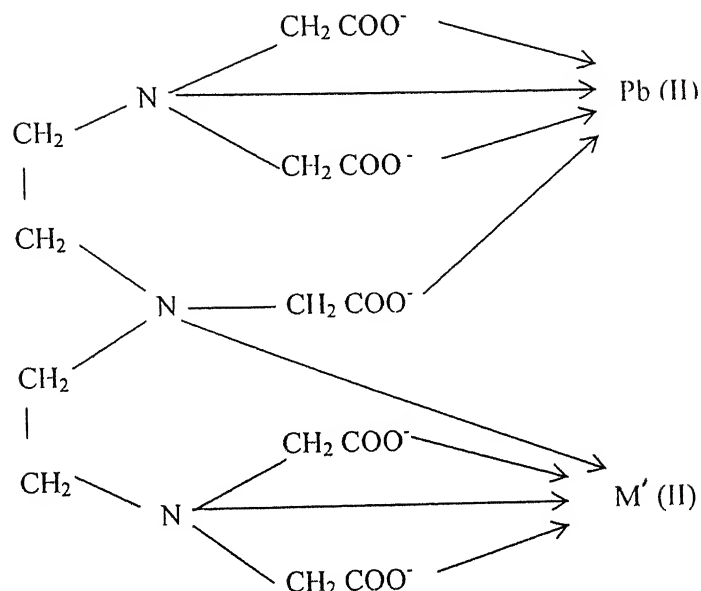


Fig. 7 Proposed Structure of Pb (II) –DTPA-M'(II) complex
Where $M' = Be(II), Cd(II)$.

The proposed structures of these mixed metal chelates seem to be convincing, because stereochemistry of the compound like $Na_2Mg(II) EDTA, x H_2O$, $Ba(II)-Cu(II)-EDTA, 5 H_2O$ have already been established and are reported in the literature

Some physical parameters for the alkaline earth metals are given in Table Fig and detect the $\log \beta$ value of the ternary system vs. Atomic number and $1/r$ of alkaline earth and transition metal ions in $Zn(II) -DTPA-$ alkaline earth metal system. Similarly Fig and detect the $\log \beta$ value of the ternary system vs. Atomic number and $1/r$ of alkaline earth metal ions in $Pb(II) -DTPA-$ alkaline earth metal system. An interesting feature of the

stability constants may be observed in these heterobimetallic complexes. Where $\log \beta$ decreases with increase in atomic number it increases with increase in the potential value i.e. (charge/size), charge being the same in all the cases.

Some Physical Parameters For The Secondary Metal Ions.						
Element with At no	Charge	Ionic Radius Å	Charge/Radi- us =Ionic Potential	Ionization potential (E) in (eV)		Electro- negativity of M (II) ion
				1 st	2 nd	
₄ Be	+2	0.34	5.88	9.3	18.2	1.5
₁₂ Mg	+2	0.78	2.56	7.6	15.0	1.2
₂₀ Ca	+2	0.99	1.89	6.1	11.9	1.0
₃₈ Sr	+2	1.13	1.20	5.69	10.98	1.0
₅₆ Ba	+2	1.35	1.00	5.21	9.95	0.9
₂₇ Co	+2	0.82	2.43	7.90	17.5	1.8
₂₈ Ni	+2	0.78	2.56	7.60	18.2	1.8
₂₉ Cu	+2	0.72	2.78	7.70	20.3	1.9
₃₀ Zn	+2	0.70	2.82	7.65	21.2	1.2
₄₈ Cd	+2	0.97	2.06	9.0	16.8	1.7
₈₂ Pb	+2	1.20	2.38	7.4	15.0	1.8

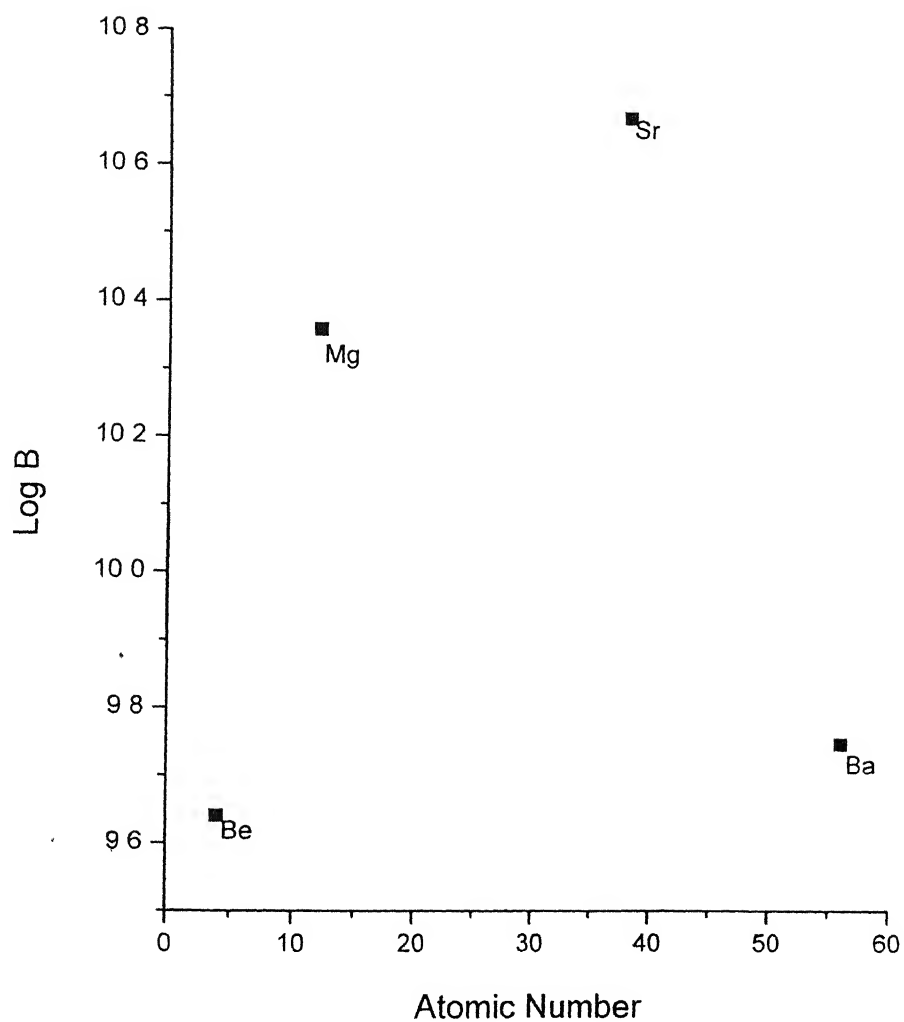


Fig. 6. Composit Irving Williams plot of log B
M(II)-DTPA (2:1) Homobimettalic Systems
Where M(II)=Be(II),Mg(II),Sr(II) and Ba(II).

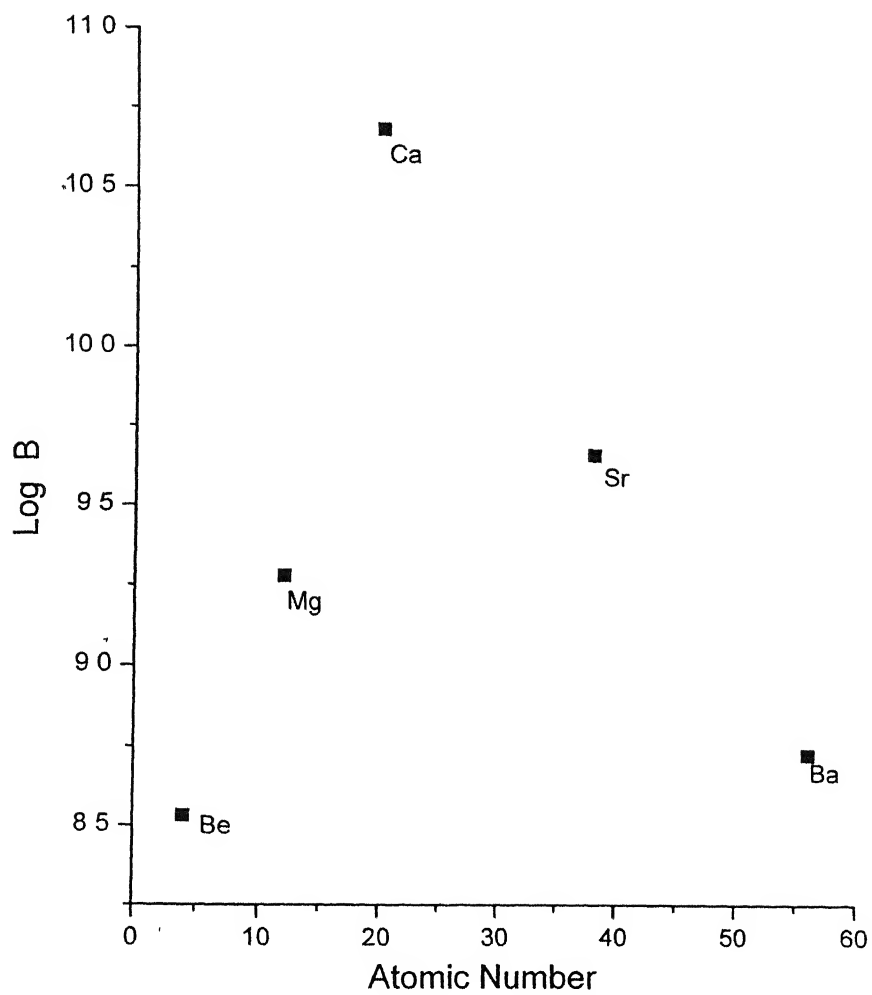


Fig 6 Composit Irving-Williams plot of log B
M(II)-DTPA (1:1) Binary Systems
Where M(II)=Be(II),Mg(II),Ca(II),Sr(II) and Ba(II)

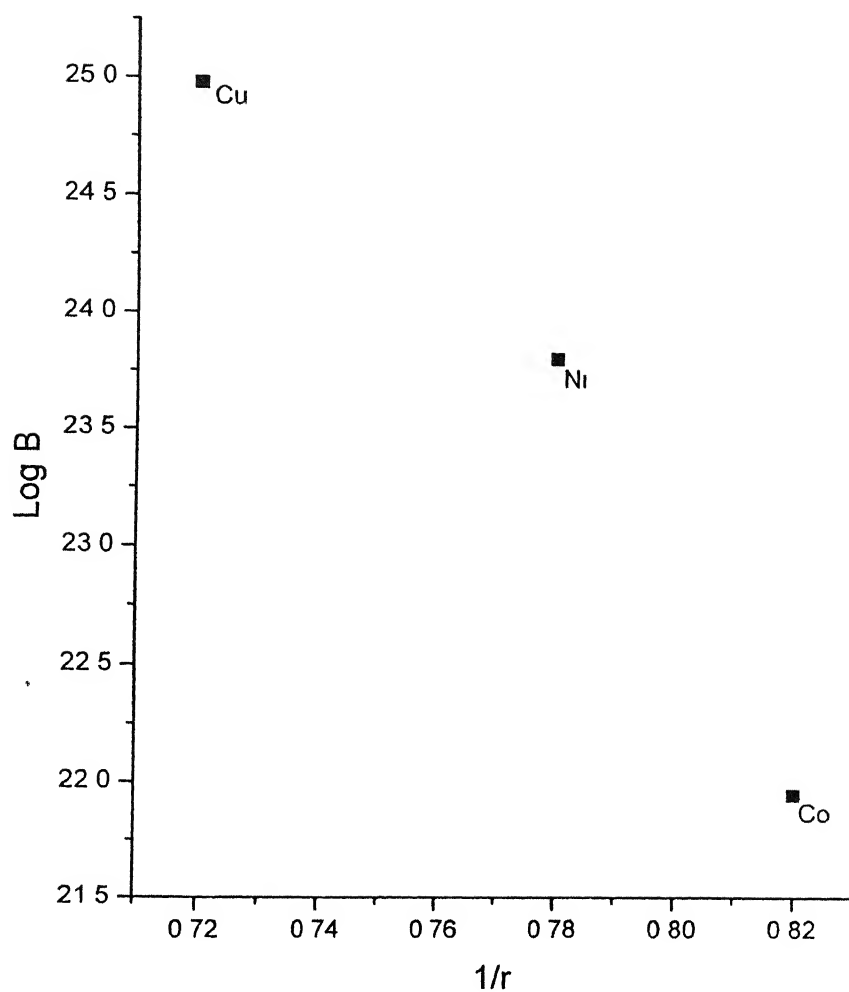


Fig. 6. Correlation of Log B with $1/r$ of Transition metals of Zn(II)-DTPA-M(II) (1:1:1) ternary systems. Where M(II)=Co(II), Ni(II) and Cu(II).

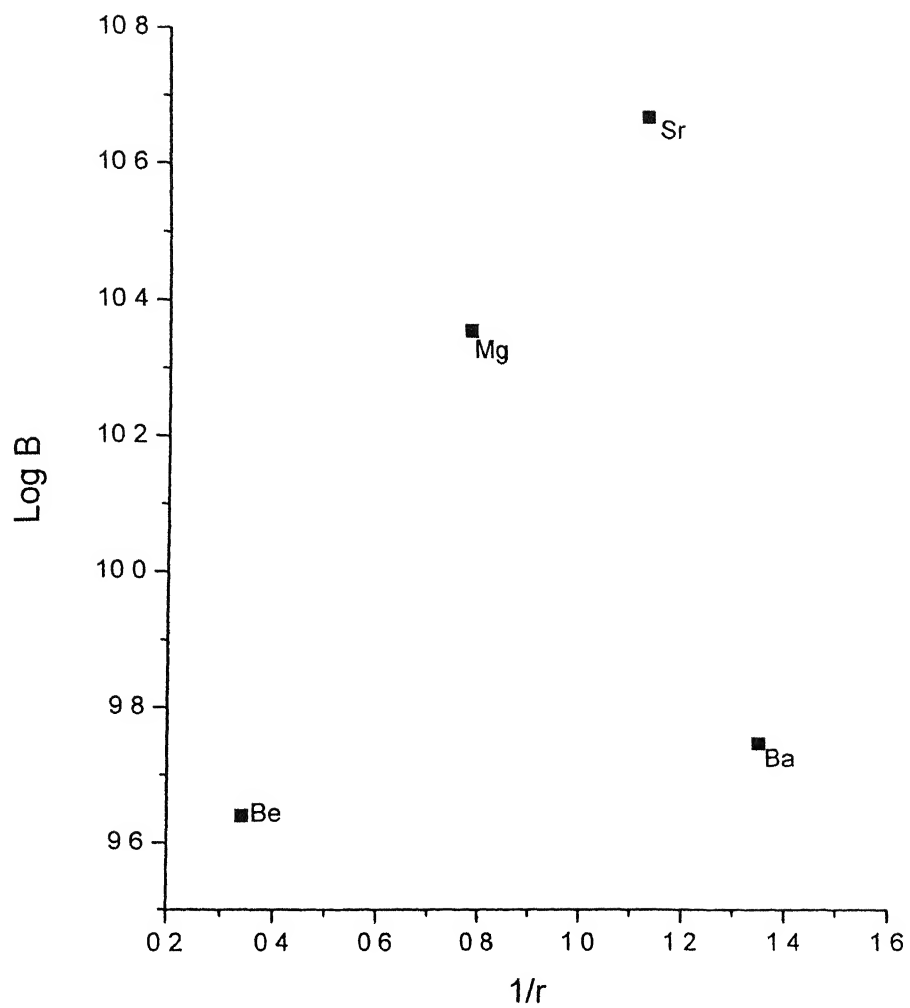


Fig 6 Correlation of Log B with 1/r of alkaline earth metals of M(II)-DTPA(2 1) Homobimetallic Systems
Where M(II)=Be(II),Mg(II),Sr(II) and Ba(II)

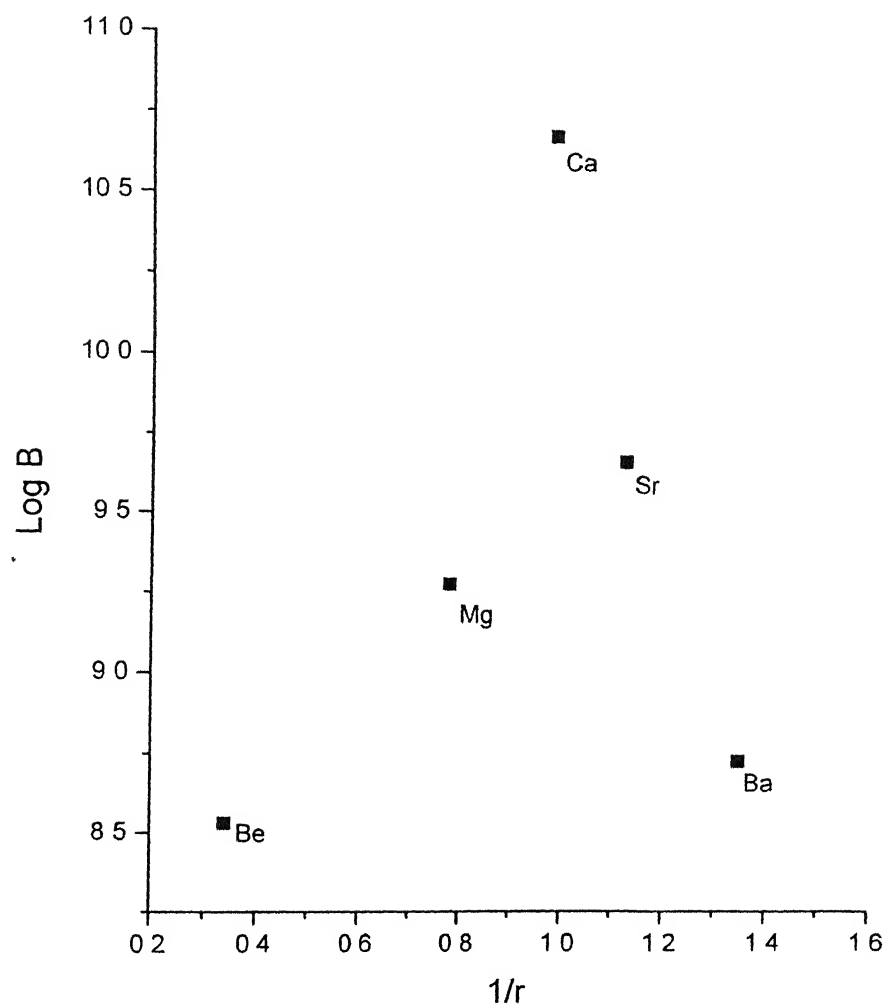


Fig 6 Correlation of Log B with $1/r$ of alkaline earth metals of M(II)-DTPA Systems Where M(II)=Be(II), Mg(II), Ca(II), Sr(II), and Ba(II)

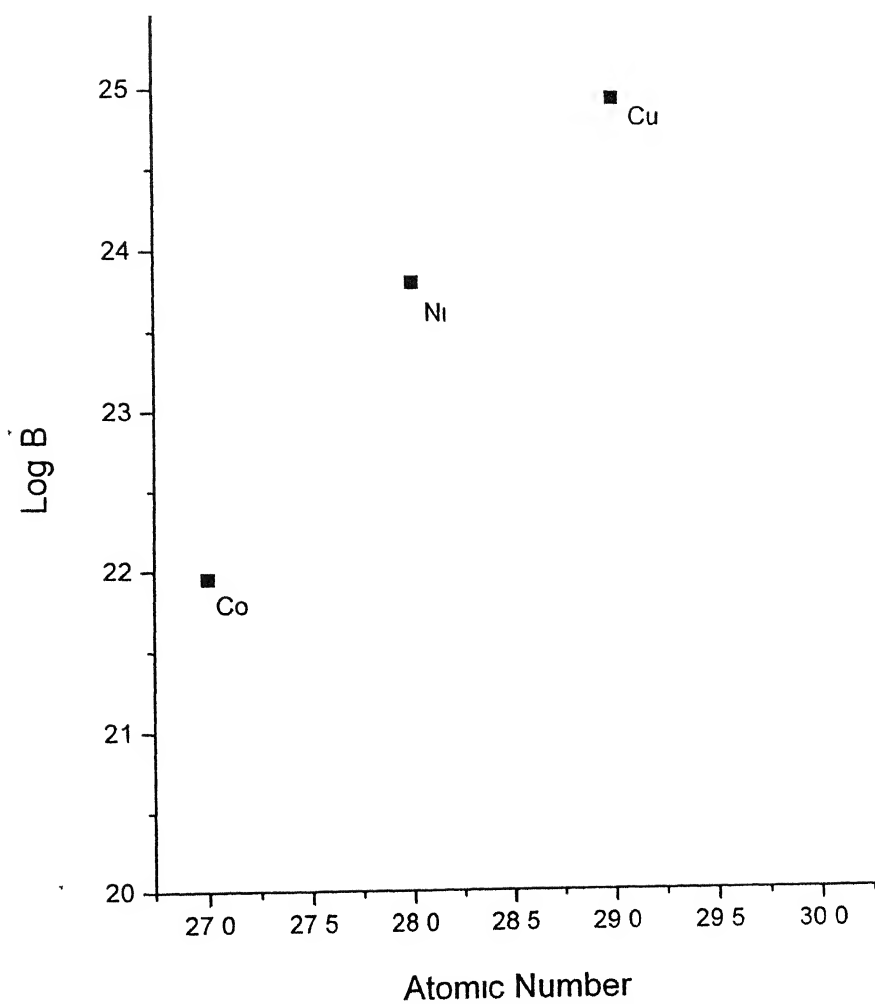


Fig 6 Composit Irving-Williams plot of log B
 Zn(II)-DTPA-M(II) (1 1 1) Ternary Systems
 Where M(II)=Co(II), Ni(II) and Cu(II)

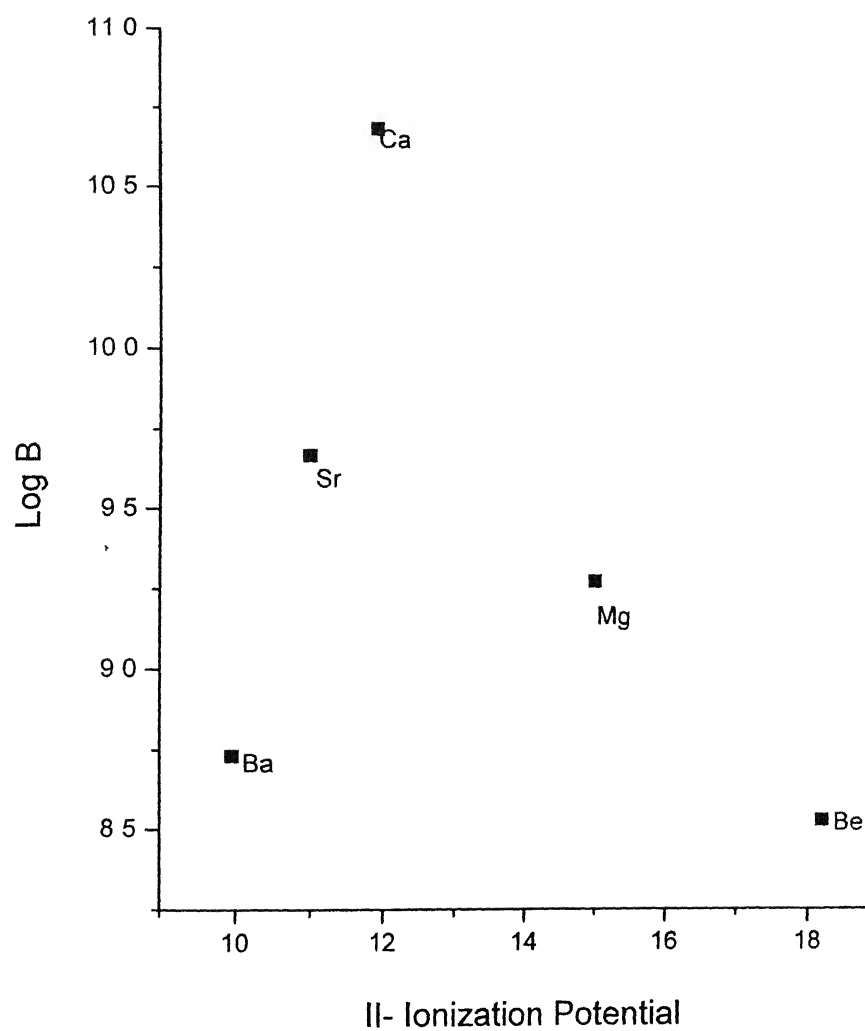


Fig. 6 Correlation of Log B with II- Ionization Potential of alkaline earth metals of M(II)-DTPA(1:1) Binary systems

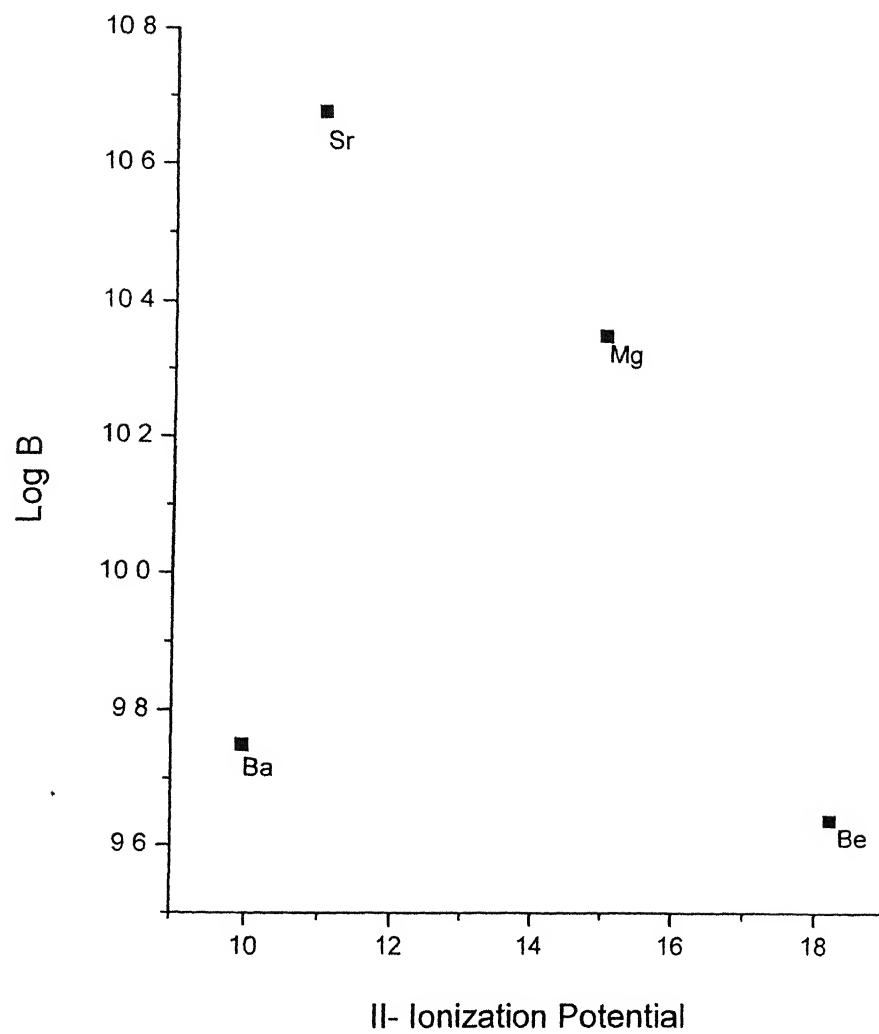


Fig 6 Correlation of Log B with II-Ionization Potential of alkaline earth metals of M(II)-DTPA(2:1) Homobimetallic system

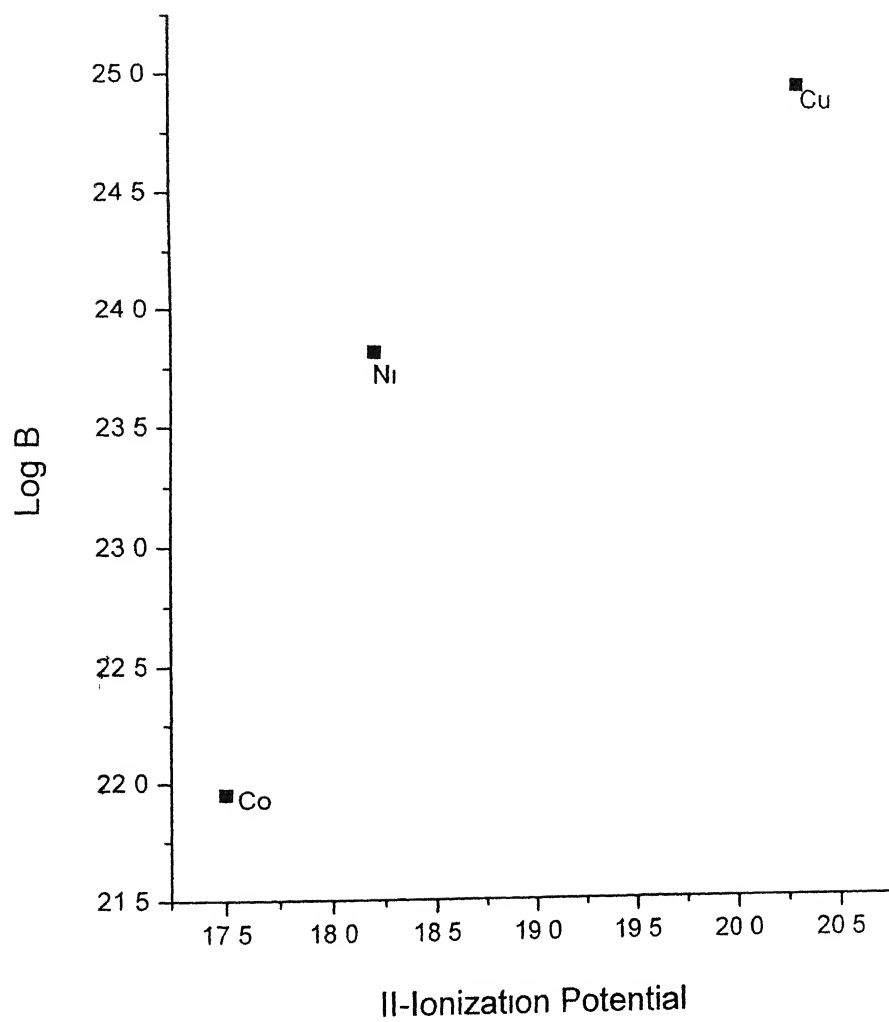


Fig 6 Correlation of Log B with II-Ionization Potential of
Transition metals of Zn(II)-DTPA-M(II) (1 1 1) ternary system

APPENDIX

1.1 PREPARATION, ANALYSIS AND IR STUDIES OF Zn (II) DTPA ALKALINE EARTH METAL COMPLEXES -

Following complexes have been prepared and studied under this section

- (1) $\text{H}_3 \text{Zn (II) -DTPA}$
- (2) $\text{Zn (II) - DTPA -Mg (II)}$
- (3) $\text{Zn (II) - DTPA -Ca (II)}$
- (4) $\text{Zn (II) - DTPA -Sr (II)}$
- (5) $\text{Zn (II) - DTPA -Ba (II)}$

Method of Preparation: -

It was noted that the above chelates can easily be prepared by reacting the appropriate amount of ligand DTPA and the metal salts in requisite amount by keeping the molar ratio as 1 1 1. Initially requisite amount of the ligand DTPA solution and Zinc metal ion in 1 1 ratio are dissolved and then finally the second metal ions (Mg, Ca, Sr and Ba) are introduced in the earlier prepared solution in requisite amount by keeping the molar ratio as 1 1:1. The method of preparation of these chelates has been described below

(1) $\text{Zn(II)-DTPA-Mg(II)}$ Complex:-

0.01 moles of ligand DTPA and 0.01 moles of Zinc oxide were taken in a beaker. 20 ml of distilled water was added into it. The solution was heated on water bath with continuous stirring for one and a half hour at 50 °C. A clear colourless solution is obtained. 0.01 moles of magnesium carbonate was weighed and added into the solution, and again it was stirred for two hours at 50 °C. The pH of the solution was adjusted between 2 to 3. A clear solution was again obtained. Its volume was reduced to half by putting it on a water bath and after cooling it was kept inside a dessicator. Light yellow coloured crystals appeared at the bottom of the beaker after ten days. It was

filtered over a buchner funnel, washed with ethanol and dried in the electric oven at 50 °C

Yield = 3.113 gm

(2) Zn(II)-DTPA-Ca(II) Complex -

0.01 moles of DTPA and 0.01 moles of Zinc oxide were weighed and taken into a beaker. 20 ml of distilled water was added into it. The solution was heated on water bath with continuous stirring for one and half hour at 70 °C. A clear colourless solution is obtained. Then 0.01 moles of calcium carbonate was weighed and added into this solution. The pH of the solution was adjusted between 2 to 3. It was again stirred for two hours at 70 °C. A clear solution again obtained. Its volume was reduced to half by putting it on a water bath and after cooling it was kept inside a dessicator. A Light yellow coloured crystals appeared at the bottom of the beaker after seven days. It was filtered over a buchner funnel, washed with ethanol and dried in the electric oven at 70 °C.

Yield = 3.129 gm

(3) Zn(II)-DTPA-Sr(II) Complex:-

0.01 moles of DTPA and 0.01 moles of Zinc oxide were weighed and taken into a beaker. 20 ml of distilled water was added into it. The solution was heated on water bath with continuous stirring for one and half hour at 80 °C. A clear colourless solution is obtained. 0.01 moles of strontium carbonate was further added to the solution. The solution was again stirred for four hours at 80 °C. A clear solution again obtained. The pH of the solution was adjusted between 2 to 3. After this its volume was reduced to half by putting it on a water bath and after cooling it was kept inside a dessicator. Light yellow coloured crystals

appeared at the bottom of the beaker after few days. It was filtered over a buchner funnel, washed with ethanol and dried in the electric oven at 80 °C

Yield = 3.148 gm

(4) Zn(II)-DTPA-Ba(II) Complex:-

0.01 moles of DTPA and 0.01 moles of Zinc oxide were weighed and taken into a beaker. 20 ml of distilled water was added into it. The solution was then heated on water bath with continuous stirring for one and half hour at 70 °C. A clear colourless solution is obtained. 0.01 moles of barium carbonate was again added into this solution. The pH of the solution was adjusted between 2 to 3. It was further stirred for four hours at 90 °C. A clear solution was again obtained. Its volume was reduced to half by putting it on a water bath and after cooling, it was kept inside a dessicator. Light yellow coloured crystals appeared at the bottom of the beaker after ten days. It was filtered over a buchner funnel, washed with ethanol and dried in the electric oven at 90 °C

Yield = 3.150 gm

Analysis:-

The analysis of carbon, hydrogen and nitrogen were done using Heracus Carlo Erba 1108 in the Regional Sophisticated Instrumentation Center, Central Drug Research Institute, Lucknow.

The analysis of metal ions in the complexes were carried out by standard methods⁽²⁰¹⁻²⁰²⁾. 0.2 gm of the complex was weighed and taken together with 10 ml of aquaregia solution in a small beaker. The solution was evaporated to dryness on water bath. This procedure was repeated 2-3 times to decompose the complex completely. The residue was dissolved in 10-20 ml of 1 N HCl. In another beaker 2N-

-NaOH solution was prepared and H₂S gas was passed for about 10 minutes to prepare sodium sulphide solution. This solution thus prepared was added to the previous solution, to get the black precipitate, which reappears, in acidic medium. The mother liquor was boiled for 10 to 15 minutes and kept as such for one hour. The black precipitate was filtered in sintered glass crucible, thoroughly washed 2-3 times with double distilled water. The filtrate and washings were collected together and were used for the estimation of the second metals. The Zinc sulphide precipitate was again washed twice with ethanol, twice with 5-10 ml of carbondisulphide solution and finally with ethanol. The precipitate was dried in an electric oven at 60-70 °C. It was weighed and thus the amount of copper metal was estimated by EDTA titration methods, by using appropriate indicator solutions.

The results of the analysis as well as physical properties are listed in table

INFRA- RED SPECTROSCOPY

Fourier transform infra-red spectra of the ligand DTPA, H₃ Zn (II) DTPA and, H₃ Pb (II) DTPA of heterobinuclear chelates were recorded in the region 400-4000 cm⁻¹ in Nujol mulls/KBr disc/ CsI/ CHCl₃ with the help of Shimadzu Spectrophotometer, model 820 IPC at the Regional Sophisticated Instrumentation Center, Central Drug Research Institute Lucknow and are shown in fig 1,2. Table contains the important characteristic infra-red-absorption frequencies of the ligand DTPA and its heterobinuclear complexes.

The main infra-red absorption peaks observed for DTPA are at (I) 3495.2 cm⁻¹ (II) 3024.0 cm⁻¹ (III) 2773.4 cm⁻¹ (IV) 1732.0 cm⁻¹ and (V) 1218.9 cm⁻¹. These absorption peaks represent (I) H₂O or ROH vibration (II) -CH vibration (III) -OH (carboxyl group) vibration (IV) & (VI) -C=O

(Strech- Carboxyl group) vibration as per observation of Morris & Busch⁽²⁰³⁾

The peaks observed for H₃ Zn (II) DTPA are at (I) 3417.2 cm⁻¹ (II) 3020.2 cm⁻¹ (III) 2770.4 cm⁻¹ (IV) 1690.0 cm⁻¹ (V) 1621.0 cm⁻¹ (VI) 1220.9 cm⁻¹. These absorption peaks represent (I) H₂O or ROH vibration (II) -CH vibration (III) -OH (carboxyl group) vibration (VI)- COOM vibration &(V) -C=O (Strech- Carboxyl group) vibration. As compared to corresponding to free carboxylic group at 1700-1720 cm⁻¹. As compared to DTPA Presence of additional vibration at 1620.0 cm⁻¹ confirms the presence of - COOM vibration

The peaks observed for Zn (II)- DTPA -Mg (II) complex are at (I) 3380.2 cm⁻¹ (II) 2980.7 cm⁻¹ (III) 2775.0 cm⁻¹ (IV) 1578.5 cm⁻¹ (V) 1218.7 cm⁻¹. These absorption peaks represent (I) H₂O or ROH vibration (II) -CH vibration (III) -OH (carboxyl group) vibration (IV)- COOH vibration (V) - C=O (Strech- Carboxyl group) vibration. There is no vibration corresponding to free carboxyl group at 1700 cm⁻¹. Whereas this vibration is present in Zn (II) DTPA complex as compared to DTPA the presence of additional vibration at 1681.5 cm⁻¹. Confirms the presence of - COOM vibration

The peaks observed for HCa (II) Zn (II) - DTPA are at (I) 3430.9 cm⁻¹ (II) 2964.4 cm⁻¹ (III) 2774.2 cm⁻¹ (IV) 1616.2 cm⁻¹ (V) 1257.5 cm⁻¹. These absorption peaks represent (I) H₂O or ROH vibration (II) -COOM vibration &(V) -C=O (Strech- Carboxyl group) vibration. As compared to H₃ Zn(II) DTPA there is no vibration corresponding to free carboxyl group at 1700 cm⁻¹. As compared to DTPA Presence of additional vibration at 1591.2 cm⁻¹ confirms the presence of - COOM vibration

Table 1

PHYSICAL PROPERTIES AND ANALYTICAL DATA OF COMPLEXES

Formula	Colour	Decomposition on temp ($^{\circ}\text{C}$)	Analysis (experimental)					Analysis (Theoretical)				
			Carbon	Hydrogen	Nitrogen	Zinc	Ind metal	Carbon	Hydrogen	Nitrogen	Zinc	Ind metal
Zn(II) DTPA	Light Yellow	188 $^{\circ}\text{C}$	24.48	3.36	7.95	29.72	4.10	25.87	2.93	6.43	30.82	3.68
Zn (II)-DTPA -Mg (II).2H ₂ O	Light Yellow	192 $^{\circ}\text{C}$	25.19	3.08	6.92	30.11	5.22	25.27	2.86	6.31	30.16	6.02
Zn (II)-DTPA -Ca (II).2H ₂ O	Light Yellow	194 $^{\circ}\text{C}$	22.03	2.58	4.66	27.47	13.74	23.58	2.27	5.51	28.08	12.28
Zn (II)-DTPA - Sr (II).2H ₂ O	Light Yellow	191 $^{\circ}\text{C}$	22.87	2.59	4.67	26.75	17.92	22.05	2.48	5.49	26.32	17.98

Table 2

INFRARED ABSORPTION TABLE OF DTPA

AND

Zn(II)-DTPA-Alkaline Earth Metal Complexes

Complexes	H ₂ O or ROH	-CH	-OH	-COOH	-COOM	-COOH
Ligand DTPA	3495 2	3024 0	2773 4	1732 0	-	1218.9
Zn(II) DTPA	3417 2	3020.2	2770 4	1690 0	1621 0	1220.9
Zn (II)-DTPA -Mg (II) 2H ₂ O	3380.2	2980.7	2775 0	-	1578 5	1218.7
Zn (II)-DTPA -Ca (II) .2H ₂ O	3430.9	2964 4	2774 2	-	1616 2	1257 5
Zn (II)-DTPA - Sr (II) .2H ₂ O	3402.2	2964.5	2625 5	-	1585 5	1260.5
Zn (II)-DTPA- Ba (II) 2H ₂ O	3425 5	2859.5	2681 5	-	1592.5	1258.5

1.2 PREPARATION, ANALYSIS AND IR STUDIES OF Pb (II) – DTPA –ALKALINE EARTH METALS COMPLEXES:-

This section deals with the preparation, analysis and IR studies of Pb (II) – DTPA – alkaline earth metals heterobimetallic complexes. Following heterobimetallic chelates are discussed in this section:

- (1) **Pb (II)- DTPA**
- (2) **Pb (II) –DTPA- Mg (II)**
- (3) **Pb (II) –DTPA- Ca (II)**
- (4) **Pb (II) –DTPA- Sr (II)**
- (5) **Pb (II) –DTPA- Ba (II)**

These chelates are also prepared by reacting the appropriate amount of ligand DTPA initially with lead metal ion keeping the ratio as 1:1, then second metal ions are introduced in requisite amount in the solution by keeping the molar ratio as 1:1:1. In all the cases metal salts were heated with the ligand solution to get the desired product. The method of preparation of these chelates is described below-

(1) **Pb (II) –DTPA- Mg (II) Complex: -**

0.01 moles of ligand DTPA and 0.01 moles of lead oxide were taken in a beaker; 10 ml of distilled water was added to it. The solution was heated on water bath with continuous stirring for one hour at 60 °C. The substance dissolves completely. 0.01 moles of Magnesium Carbonate (Mg CO_3) was further added into the solution, and it was stirred for two hours at 60 °C. A clear solution was again obtained. Its volume was almost reduced to half by putting it on a water bath. After cooling it was kept inside a dessicator. colourless crystals appeared at the bottom of

the beaker after several days. It was filtered over a buchner funnel, washed with ethanol and dried in the electric oven at 60 °C

Yield = 3.35 gm

(2) Pb (II) -DTPA- Ca (II) Complexes:-

0.01 moles of ligand DTPA and 0.01 moles of lead oxide were weighed taken in a beaker. 10 ml of distilled water was added to it. The solution was heated on water bath with continuous stirring for one hour at 60 °C. The substance dissolves completely. 0.01 moles of Calcium Carbonate (CaCO_3) was further added into the solution, and it was stirred for two hours at 60 °C. A clear solution was obtained. Its volume was almost reduced to half by putting it on a water bath. After cooling it was kept inside a dessicator. Yellow cloured crystals appeared at the bottom of the beaker after several days. It was filtered over a buchner funnel, washed with ethanol and dried in the electric oven at 60 °C

Yield = 3.342 gm

(3) Pb (II) -DTPA- Sr (II) Complexes:-

0.01 moles of ligand DTPA and 0.01 moles of lead oxide were taken in a beaker. 10 ml of distilled water was added to it. The solution was heated on water bath with continuous stirring for one hour at 60 °C. The substance dissolves completely. 0.01 moles of Strontium Carbonate was added into the solution, and again it was stirred for some time at 80 °C. A clear solution was obtained. Its volume was almost reduced to half by putting it on a water bath. After cooling it was kept inside a dessicator. Light yellow coloured crystals appeared at the bottom of the beaker after ten days. It was filtered

over a buchner funnel, washed with ethanol and dried in the electric oven at 80 °C

Yield = 3.352 gm

(4) Pb (II) -DTPA- Ba (II) Complexes:-

0.01 moles of ligand DTPA and 0.01 moles of Lead Oxide were taken in a beaker 10 ml of distilled water was added to it. The solution was heated on water bath with continuous stirring for an hour at 60 °C. The substance dissolves completely. 0.01 moles of Barium Carbonate was further added into the solution, and it was stirred for some time at 80 °C. A clear solution was obtained. Its volume was almost reduced to half by putting it on a water bath. After cooling it was kept inside a desiccator. White coloured crystals appeared at the bottom of the beaker after several days. It was filtered over a buchner funnel, washed with ethanol and dried in the electric oven at 80 °C

Yield = 3.370 gm

Elemental Analysis :-

The analysis of carbon hydrogen and nitrogen were done similarly by using the heracus carlo Erba 1108 in the Regional Sophisticated Instrumentation Center, Center Drug Research Institute, Lucknow.

The analysis of the metal ions in the complex was carried out by standard methods. 0.2 gm of the complex was weighed and taken together with 10 ml of aquaregia solution in a small beaker. The solution was evaporated to dryness on water bath. This procedure was repeated 2-3 times to decompose the complex completely. The residue was dissolved in 10-20 ml of 1N HCl. In another beaker 2N NaOH solution

was prepared and H_2S gas was passed for about 10 minutes to prepare Sodium Sulphide solution. This solution thus prepared was added to the previous solution to get the black precipitate of cupric sulphide. This precipitate was dissolved in excess of sodium Sulphide solution. On adding 2 N HCl, the black precipitate reappears in acidic medium. The mother liquor was boiled for 10 to 15 minutes and kept as such for one hour. The black precipitate was filtered in sintered glass crucible. Thoroughly washed 2-3 times with double distilled water. The filtrate was collected. Cupric sulphide precipitate was again washed twice with ethanol, twice with 5-10 ml of carbondisulphide solution and finally with ethanol. The precipitate was dried in a electric oven at $60-70^\circ\text{C}$. It was weighed and thus the amount of copper metal was estimated. The second metal was estimated by EDTA titration methods by using appropriate indicator solution.

The results of the analysis as well as some physical properties are listed in table

INFRA- RED SPECTROSCOPY

The infra-red spectroscopy absorption peaks observed for ligand DTPA has already been discussed in this chapter. The peaks for lead-DTPA with alkaline earth metals heterobimetallic chelates are discussed Fig. represented IR absorption spectra of these complexes. The infra-red absorption frequencies of chelates are listed in table.

The peaks for binary chelate Pb(II)-DTPA are at (I) 3395.5 cm^{-1} (II) 3045.2 cm^{-1} (III) 2630.4 cm^{-1} (IV) 1695.5 cm^{-1} (V) 1605.5 cm^{-1} and (VI) 1235.0 cm^{-1} . These peaks represent (I) H_2O or ROH vibration (II) $-\text{CH}$ vibration (III) $-\text{OH}$ (carboxyl group) vibration (IV) & (VI) $-\text{C}=\text{O}$ (Stretch-Carboxyl group) vibration and (V) $-\text{COOM}$ vibration. As compared to DTPA the presence of additional vibration at 1605.0 cm^{-1} confirms the presence of $-\text{COOM}$ vibration.

The peaks observed for Pb (II)- DTPA -Mg(II) chelate are at (I) 3418.6 cm^{-1} (II) 3038.7 cm^{-1} (III) 2736.7 cm^{-1} (IV) 1585.6 cm^{-1} (V) 1257 cm^{-1} . These peaks represent (I) H_2O or ROH vibration (II) $-\text{CH}$ vibration (III) $-\text{OH}$ (carboxyl group) there is no vibration corresponding presence of additional vibration at 1585.5 cm^{-1} confirms the presence of $-\text{COOM}$ vibration

The peaks observed for Pb (II)- DTPA -Ca (II) are at (I) 3372.0 cm^{-1} (II) 2954.0 cm^{-1} (III) 2621.0 cm^{-1} (IV) 1595.5 cm^{-1} (V) 1258.6 cm^{-1} . These peaks represent (I) H_2O or ROH vibration (II) $-\text{CH}$ vibration (III) $-\text{OH}$ (carboxyl group) vibration (IV) $-\text{COOM}$ vibration & (V) $-\text{C}=\text{O}$ (Stretch-Carboxyl group) vibration. As compared to Pb(II)-DTPA there is no vibration corresponding to free carboxyl group at 1700 cm^{-1} . As compared to DTPA the presence of additional vibration at 1595.5 cm^{-1} confirms the presence of $-\text{COOM}$ vibration.

The peaks observed for Pb (II)- DTPA -Sr (II) are at (I) 3406.0 cm^{-1} (II) 2975.0 cm^{-1} (III) 2620.0 cm^{-1} (IV) 1580.5 cm^{-1} (V) 1220.6 cm^{-1} . These peaks represent (I) H_2O or ROH vibration (II) $-\text{CH}$ vibration (III) $-\text{OH}$ (carboxyl group) vibration (IV) $-\text{COOM}$ vibration (V) $-\text{C}=\text{O}$ (Stretch-Carbonyl group). As compared to Pb(II)-DTPA there is no vibration corresponding to free carboxyl group at 1700 cm^{-1} . As compared to DTPA the presence of additional vibration at 1580.5 cm^{-1} confirms the presence of $-\text{COOM}$ vibration.

The peaks observed for Pb(II)-DTPA- Ba (II) are at (I) 3422.5 cm^{-1} (II) 2895.5 cm^{-1} (III) 2690.0 cm^{-1} (IV) 1590.5 cm^{-1} (V) 1285.0 cm^{-1} . These peaks represent (I) H_2O or ROH vibration (II) $-\text{CH}$ vibration (III) $-\text{OH}$ (carboxyl group) vibration (IV) $-\text{COOM}$ vibration and (V) $-\text{C}=\text{O}$ (Stretch-Carboxyl group) vibration. As compared to Pb (II) DTPA there is no vibration corresponding to free carboxyl group at 1700 cm^{-1} . As compared to DTPA the presence of additional vibration at 1585.4 cm^{-1} confirms the presence of $-\text{COOM}$ vibration.

Table 3

PHYSICAL PROPERTIES AND ANALYTICAL DATA OF COMPLEXES

Formula	Colour	Decomposition temp (°C)	Analysis (experimental)						Analysis (Theoretical)					
			Carbon	Hydrogen	Nitrogen	Lead	IInd meta	Carbo n	Hydroge n	Nitroge n	Lead	IInd metal		
Pb(II)-DTPA-Mg(II). 2H ₂ O	White Crystals	210°C	27.47	3.37	6.68	29.14	3.861	27.25	2.85	6.61	30.92	3.93		
Pb(II)-DTPA-Ca(II). 2H ₂ O	Light Yellow Crystals	218°C	29.13	3.09	5.88	27.21	5.27	26.13	2.91	6.43	28.98	6.08		
Pb(II)-DTPA-Sr(II). 2H ₂ O	Light Yellow Crystals	220°C	27.19	2.59	5.61	24.47	13.71	24.23	2.75	5.32	26.35	14.21		
Pb(II)-DTPA-Ba(II). 2H ₂ O	White Crystals	228°C	22.25	+ 2.61	4.62	20.47	19.18	23.83	2.51	5.01	22.18	18.81		

TABLE 4

INFRA-RED ABSORPTION TABLE OF
DTPA & Pb (II)-DTPA-Alkaline Earth Metal Complexes

Complexes	H ₂ O or ROH	-CH	-OH	-COOH	-COOM	-COOH
Ligand DTPA	3495.2	3024 0	2773.4	1732.0	-	1218.9
Pb (II) DTPA	3395 5	3045 2	2630.4	1695.5	1605 0	1235.0
Pb (II)-DTPA -Mg (II)- .2H ₂ O	3418.6	3038.7	2736.7	-	1585.6	1258.6
Pb (II)-DTPA -Ca (II) 2H ₂ O	3372.0	2954.0	2621.0	-	1595 5	1240 0
Pb (II)-DTPA - Sr (II) .2H ₂ O	3406.0	2975.0	2620.0	-	1508 5	1220 6
Pb(II)-DTPA- Ba (II) .2H ₂ O	3422.5	2895 5	2690.0	-	1590 5	1285.0



के० औ० अ० सं०
C.D.R.I.

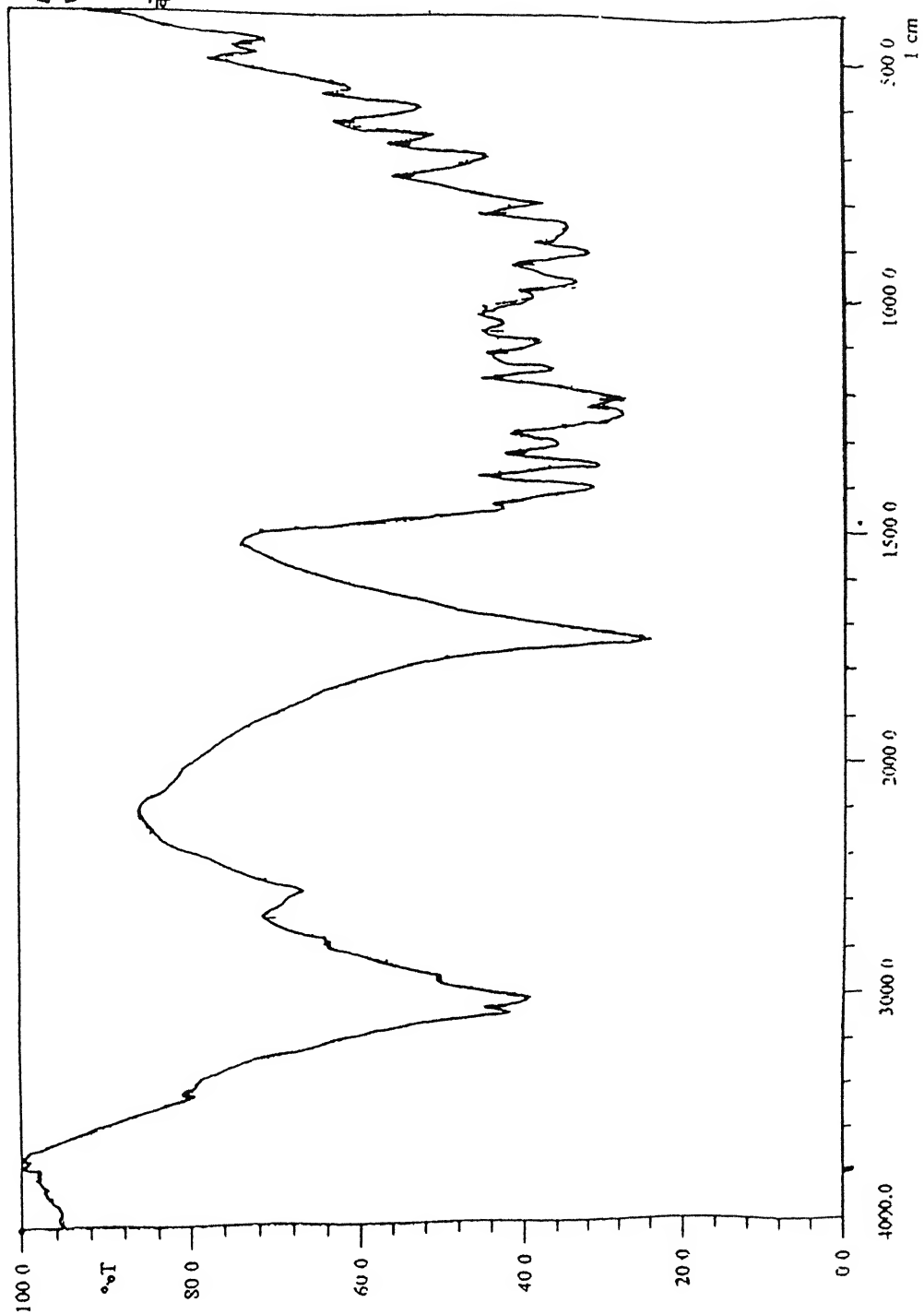


Fig 1 DTPA[Diethylenetriaminopentaacetic acid]

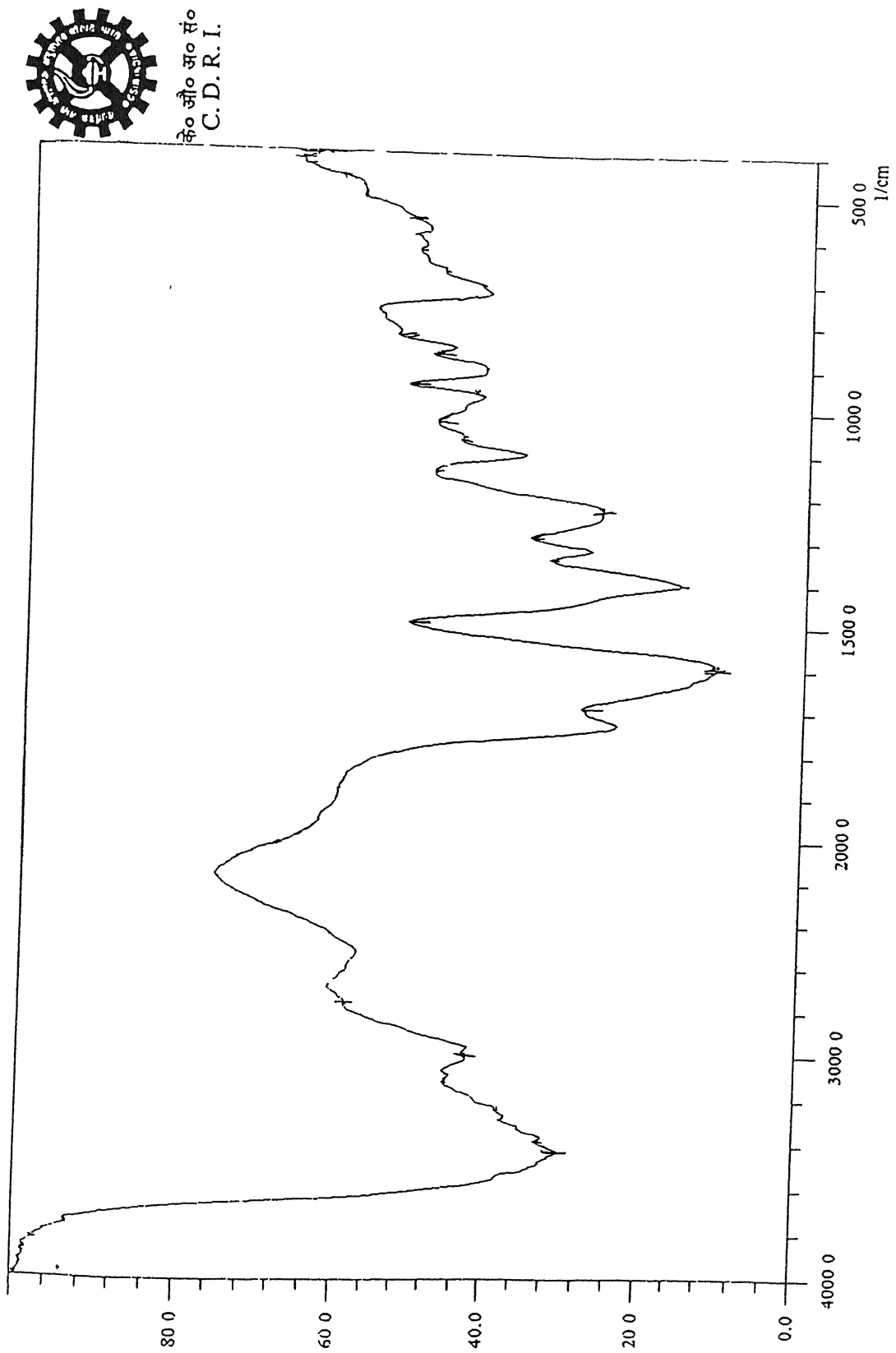


Fig 2- Zn(II)-DTPA Complex.



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C. D. R. I.

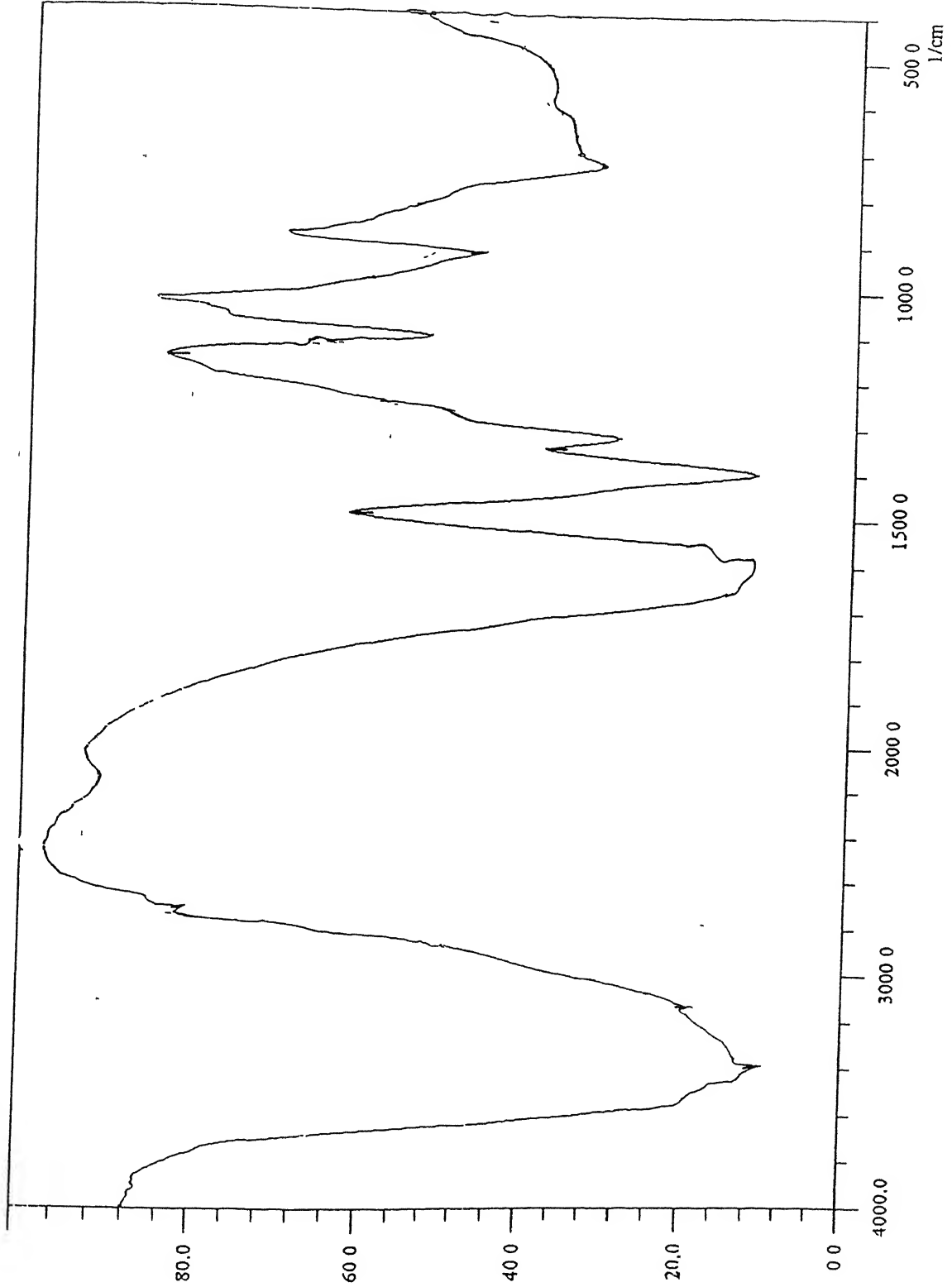


Fig. 3. Zn(II)-DTPA-Mg(II) Complex



के० औ० सं० सं०
C. D. R. I.

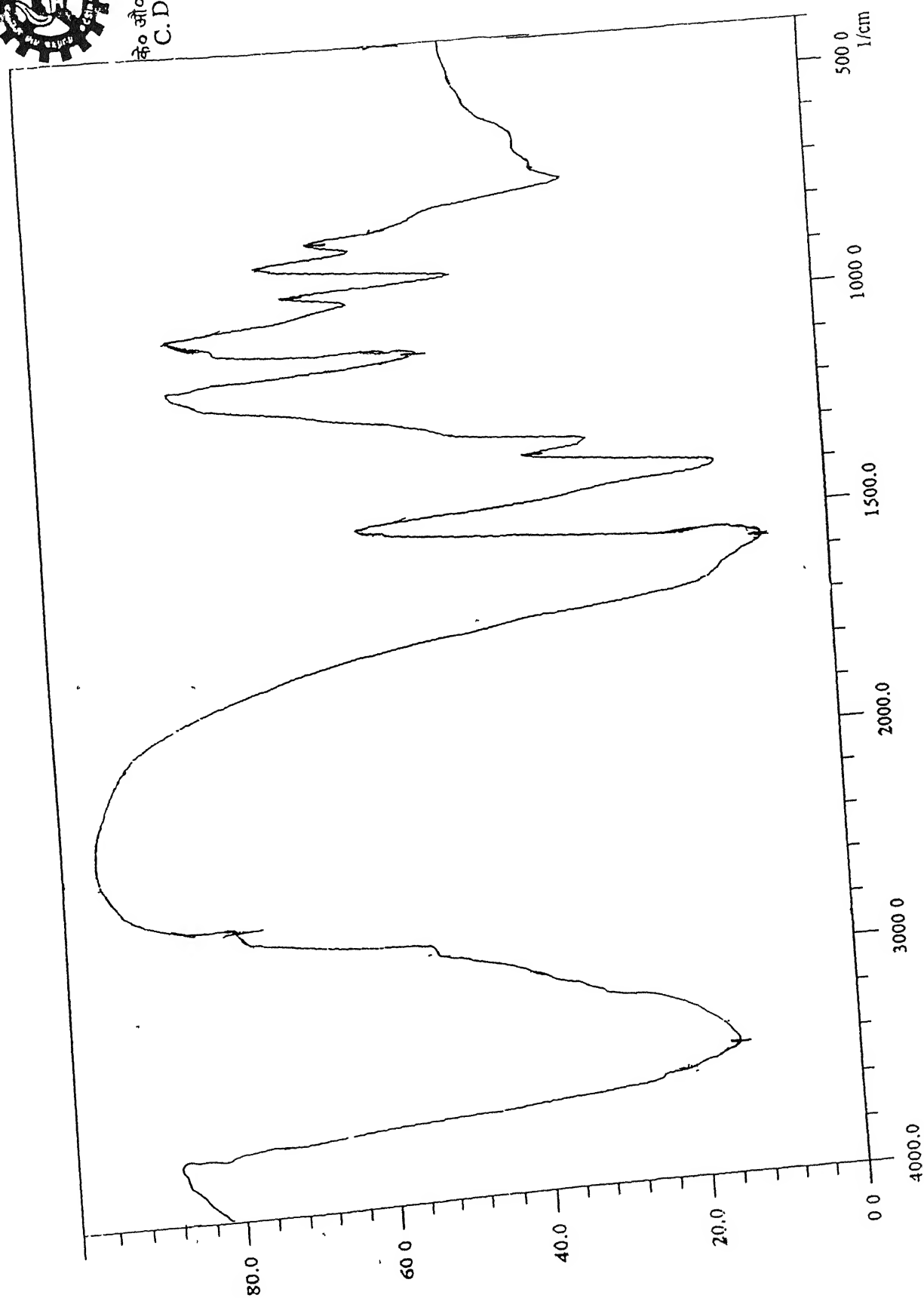


Fig. 4 Zn(II)-DTPA-Ca(II) Complex.

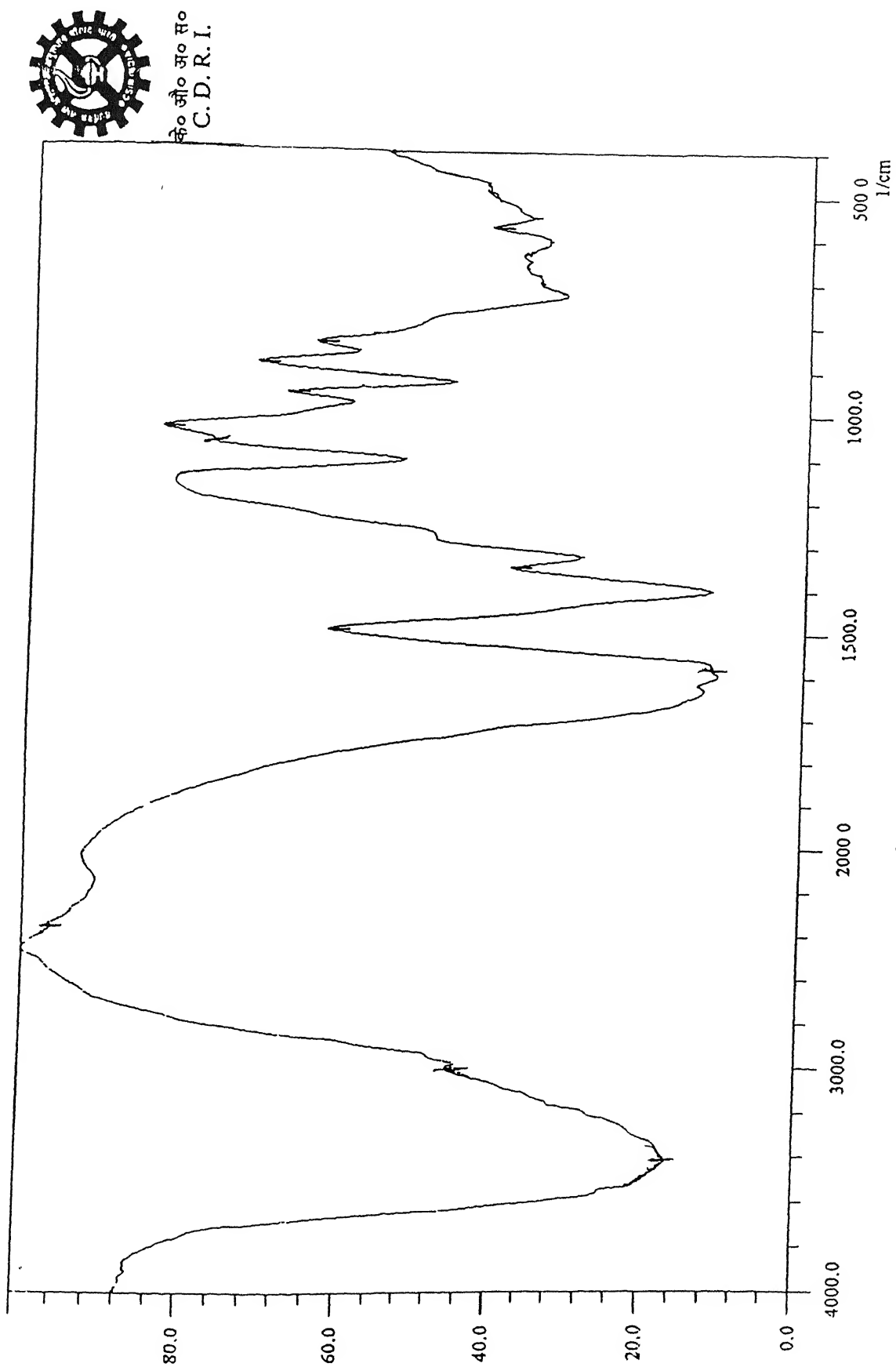


Fig 5-Zn(III)-DTPA-Sr(III) Complex.



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C.D. R. I.

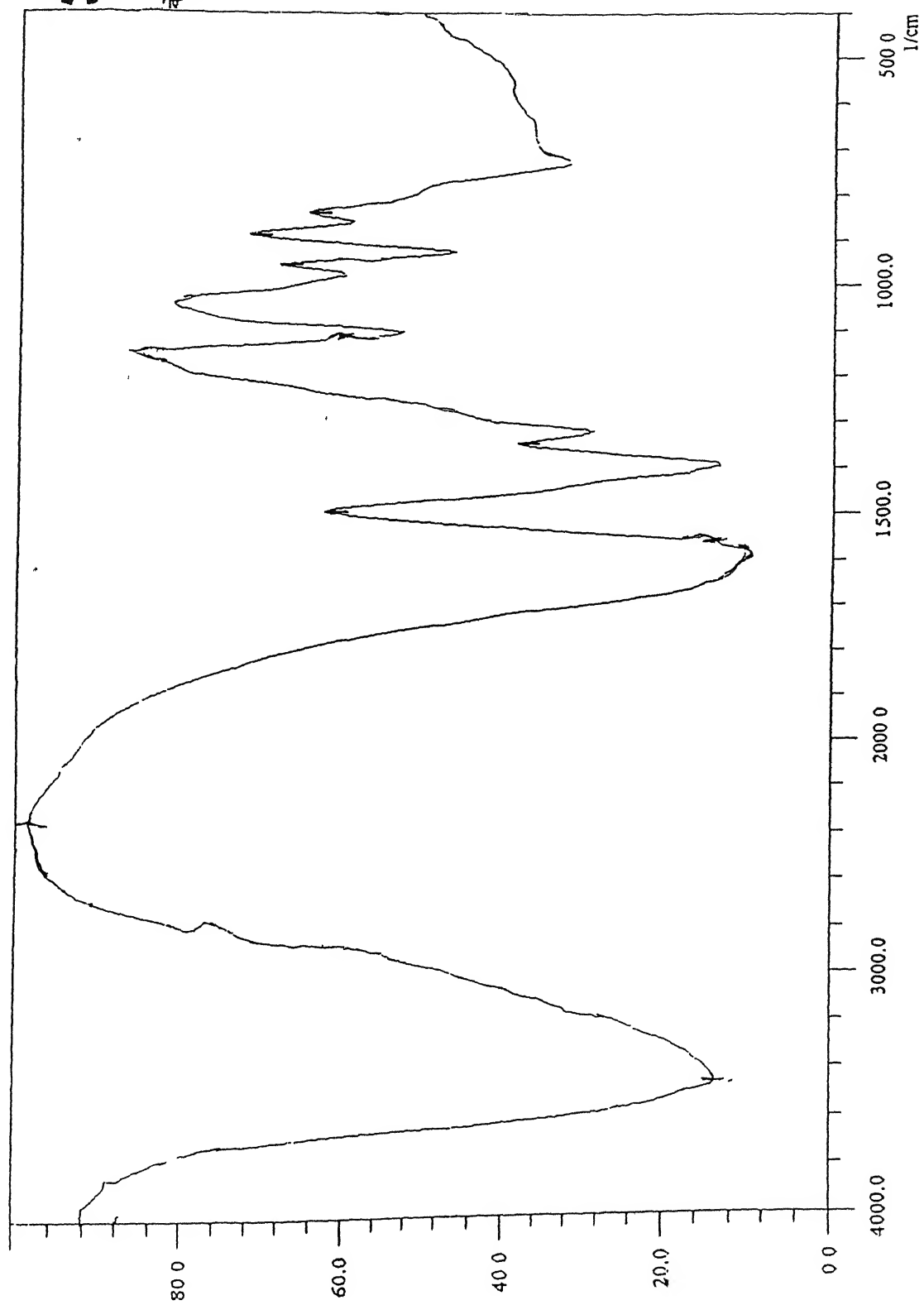


Fig 6-Zn(II)-DTPA-Ba(II) Complex.



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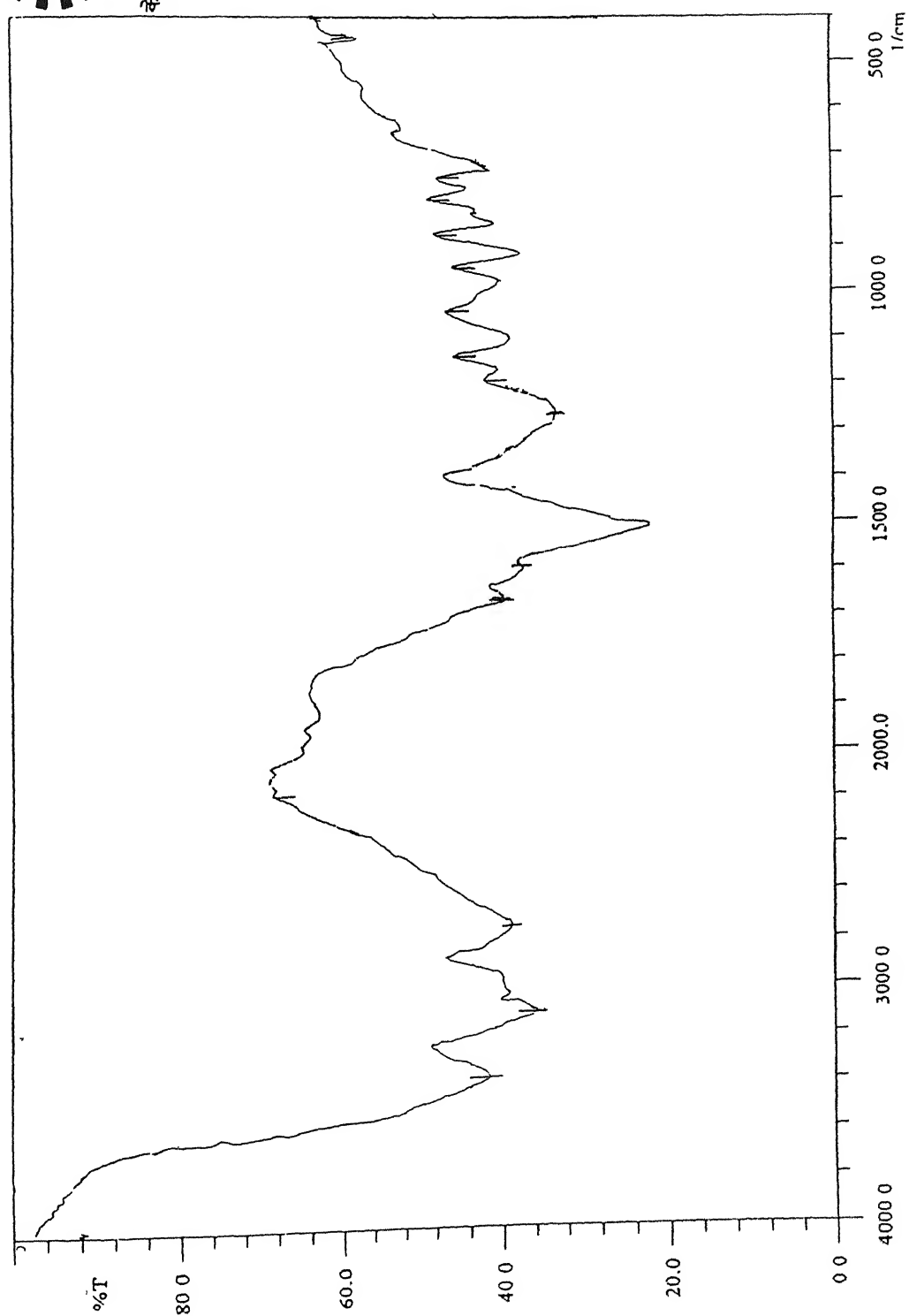


Fig 7. Pb(II)-DTPA Complex.



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C.D.R. I.

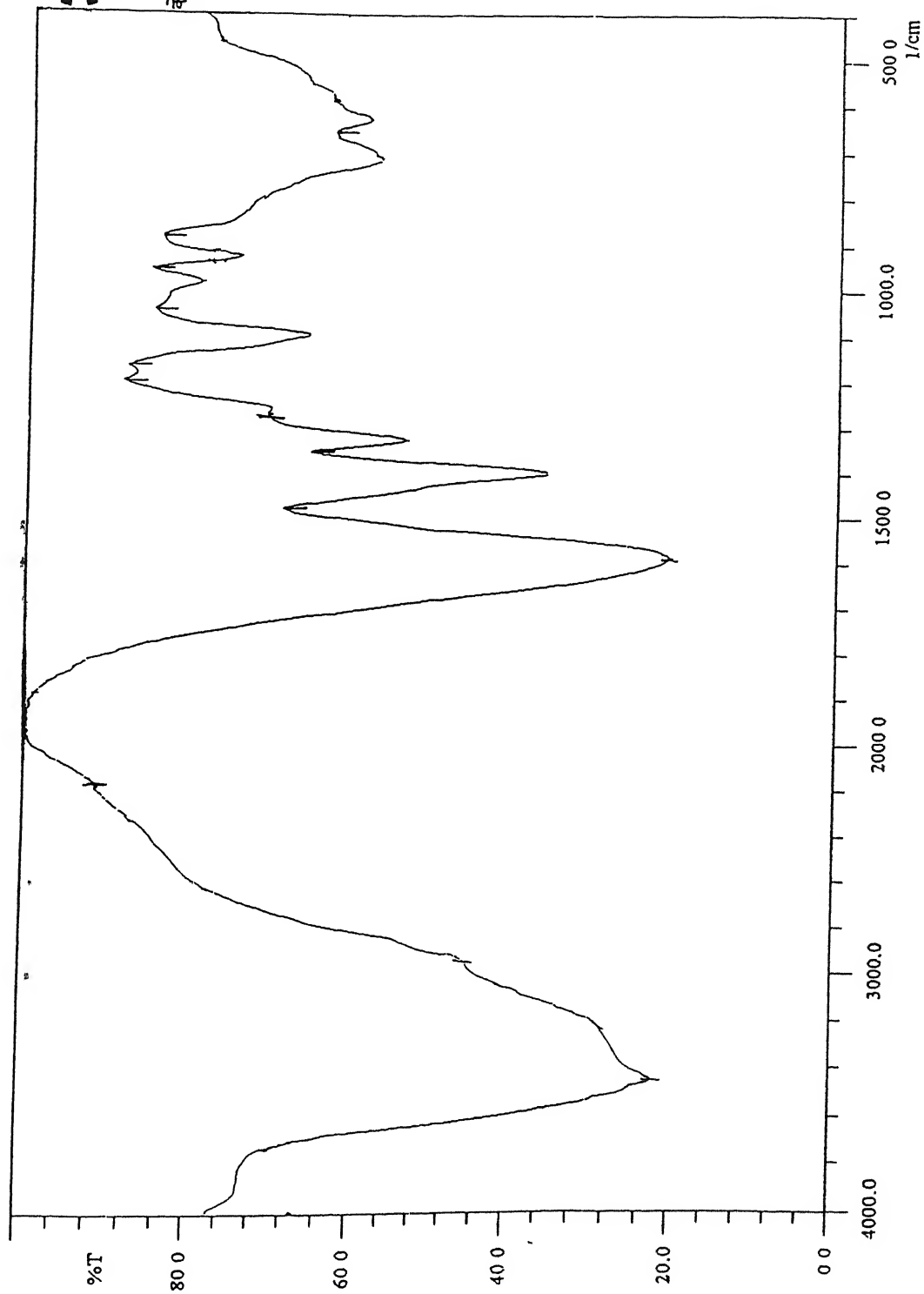


Fig. 8 Pb[II]-DTPA-Mg[II] Complex



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C. D. R. I.

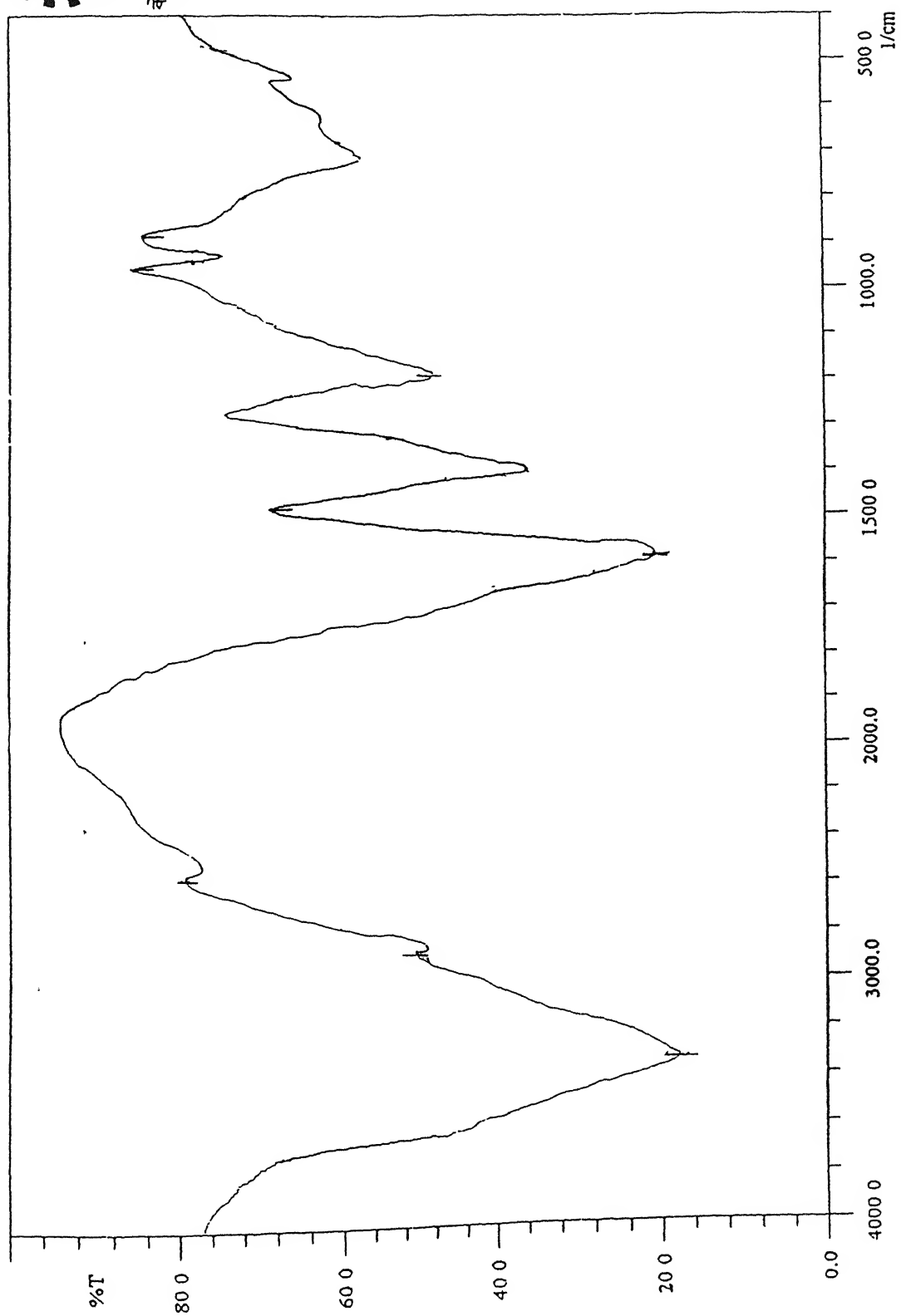


Fig. 9- Pb[II]-DTPA-Ca[II] Complex

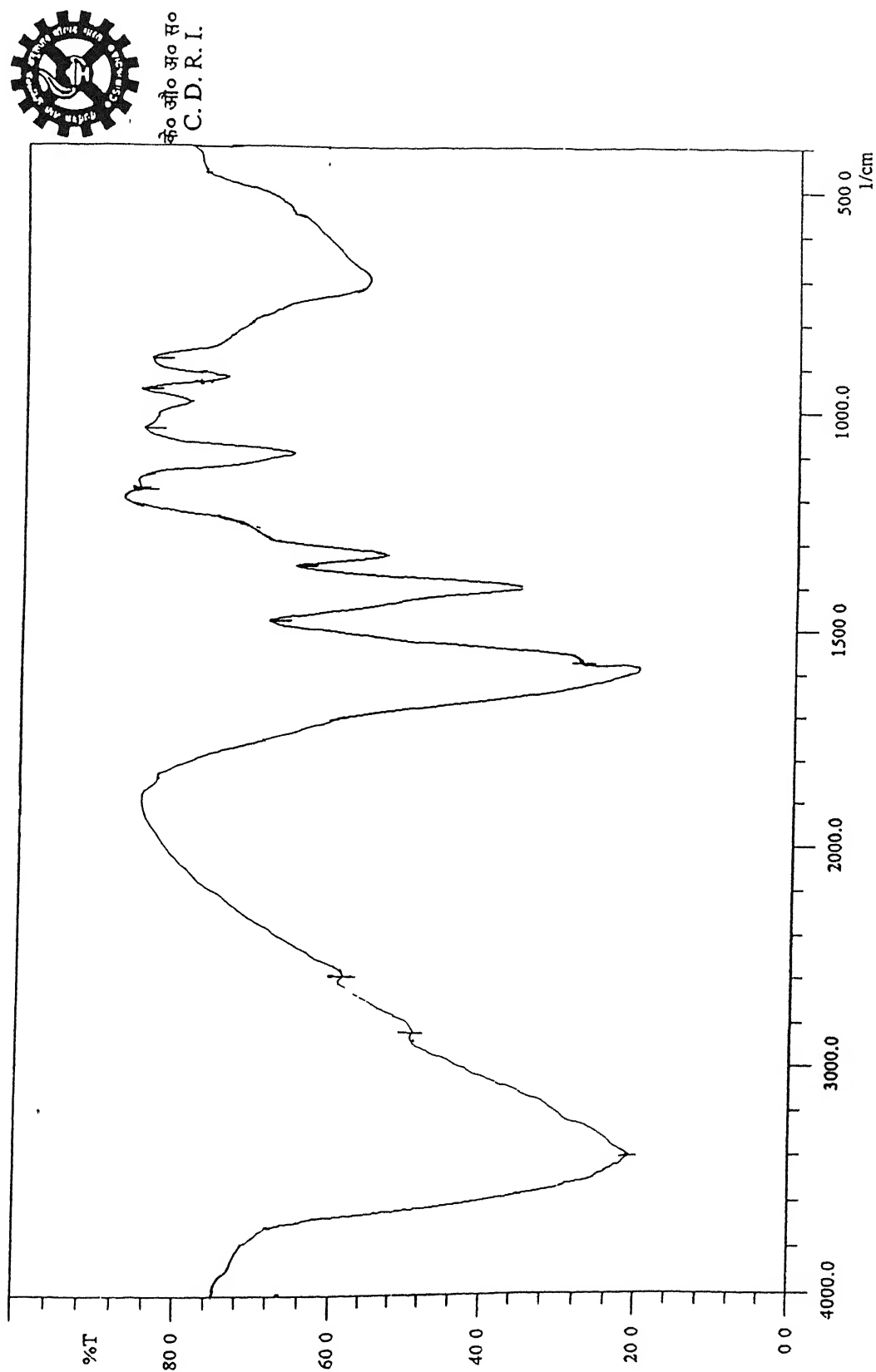


Fig 10 Pb(II)-DTPA-Sr(II) Complex

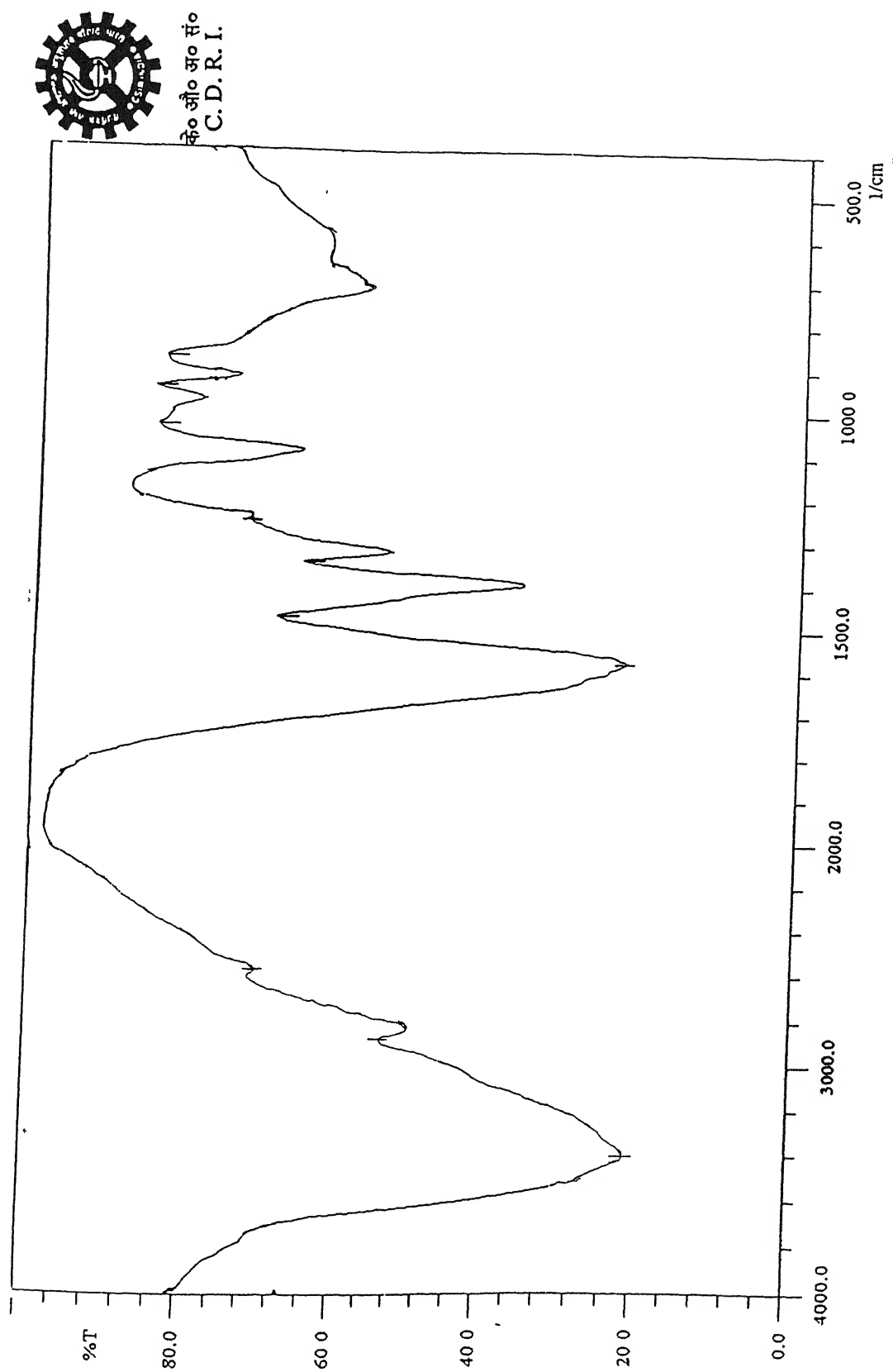


Fig 11-Pb[II]-DTPA-Ba[II] Complex

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